Electronic Supplementary Information

Acene-linked covalent organic frameworks as candidate materials for singlet fission

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Contents

1. Electronic configurations for CDFT-CI Calculations

To simulate the adiabatic low-lying excited states of most significance to the singlet fission mechanism – the S_1, charge transfer (CT), and triplet-triplet (TT) states – we followed closely the approach of Yost *et al.* in which the relevant adiabatic states are constructed from diabatic electronic states with charge and spin constraints on each acene monomer.[1] These constrained DFT (CDFT) diabatic states then provide a conveniently minimal basis in which to perform an diabatic-to-adiabatic transformation, referred to in the context of CDFT as constrained DFT-configuration interaction (CDFT-CI).[2]

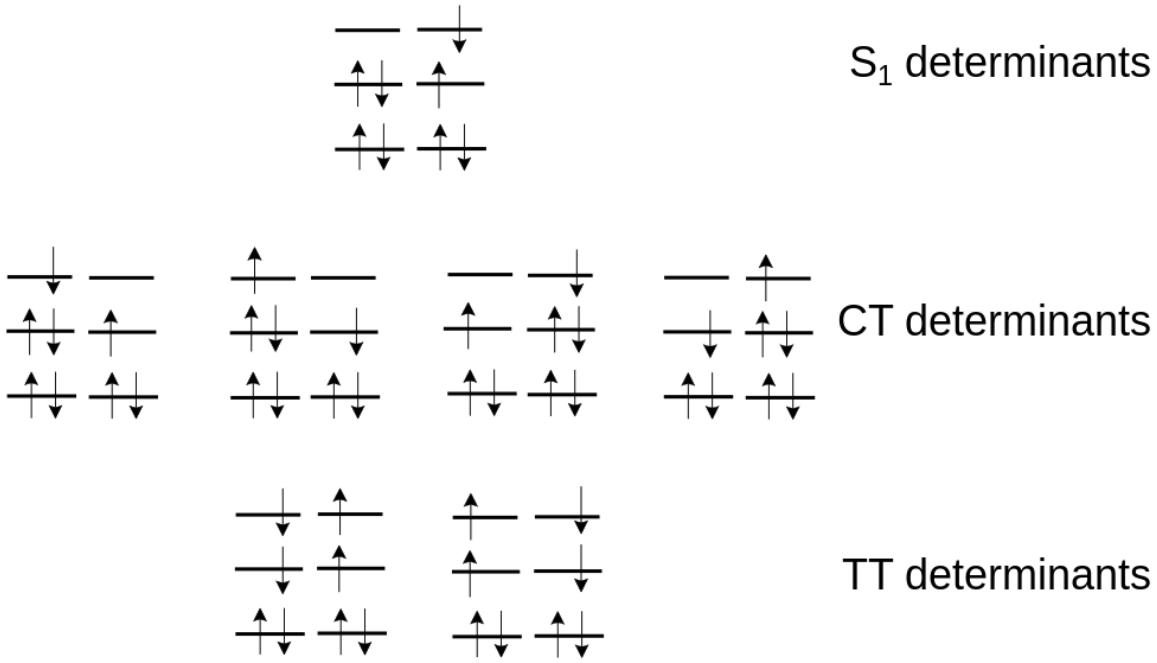

Figure S1 Molecular orbital configurations of the determinants from which S1, CT, and TT electronic energies and properties are computed.

The left and right sets of molecular orbitals in Figure S1 represent orbitals localized primarily on one or the other acene monomer. The energy of the S_1 excited state could be computed with the excitation on either monomer (only excitation of the right monomer is illustrated in Figure S1). Spin-purification of the energy of these ΔSCF excited states is accounted for by including both configurations for the excitation in the CI. Determinants involved in the construction of the CT state all have an extra electron constrained to one monomer or the other; the possible configurations with two α and two β electrons, which contribute to the lowest singlet CT state, are shown in Figure S1. Determinants considered in the construction of the triplet-triplet state are those consistent with the low-spin TT state. The overall quintet state was not included due to the highly spin-forbidden nature of singlet-to-quintet transitions.

2. Optimized interlayer distances of COF structures

Linker	AB	Serrated AA	Inclined AA	AA
Benzene	3.810	3.433	3.466	3.511
Naphthalene	3.606	3.420	3.462	3.506
Anthracene	3.423	3.407	3.479	3.506
Tetracene	3.610	3.430	3.474	3.504
Pentacene	3.612	3.437	3.484	3.503

Table S1 Interlayer stacking distances (in Angstrom) of acene-linked COFs for the four stacking patterns (perfect AB, serrated AA, inclined AA, and perfect AA) considered in this study.

3. Calculation of core-linker angular distortions

The angle observed between the plane of the acene linker and the interlayer stacking plane of the COF was determined to have a significant influence on the energetics of the acene-COF complexes, but it is not a uniquely defined quantity. We developed the following scheme to obtain internally consistent measurements of these angles:

1. Determine the Cartesian coordinates of the hydrogen and carbon atoms labeled a-g adjacent to the four vectors shown in Figure S2. The vectors $\overrightarrow{ab}$ and $\overrightarrow{gh}$ are in the plane of the COF, while the vectors $\overrightarrow{cd}$ and $\overrightarrow{ef}$ are in the plane of the acene linker.
2. Compute the angle between the COF and acene vectors on either side of the linker,

$$\overrightarrow{ab} \cdot \overrightarrow{cd} = \left\|\overrightarrow{ab}\right\| \left\|\overrightarrow{cd}\right\| \cos\theta_a$$

$$\overrightarrow{ef} \cdot \overrightarrow{gh} = \left\|\overrightarrow{ef}\right\| \left\|\overrightarrow{gh}\right\| \cos\theta_b$$

3. Take the average of the acene-COF angles obtained in step 2,

$$\theta = \frac{1}{2}(\theta_a + \theta_b)$$

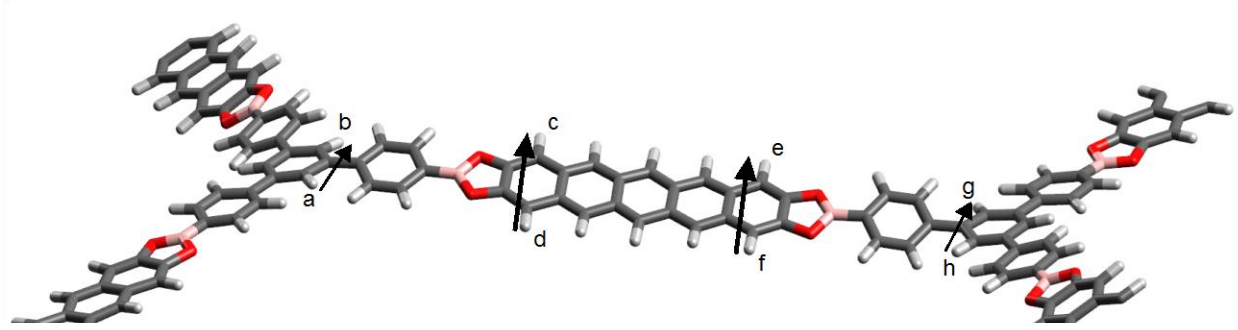

Figure S2 Vectors employed in the calculation of acene-COF angles along MD trajectories.

4. Excitation energies as a function of acene length and angle

The plot below summarizes and expands on Figure 6 in the main text by including the variation of the S_1, CT, and TT excitation energies with the acene-COF rotations θ and ϕ for all five acene-COFs investigated in this study.

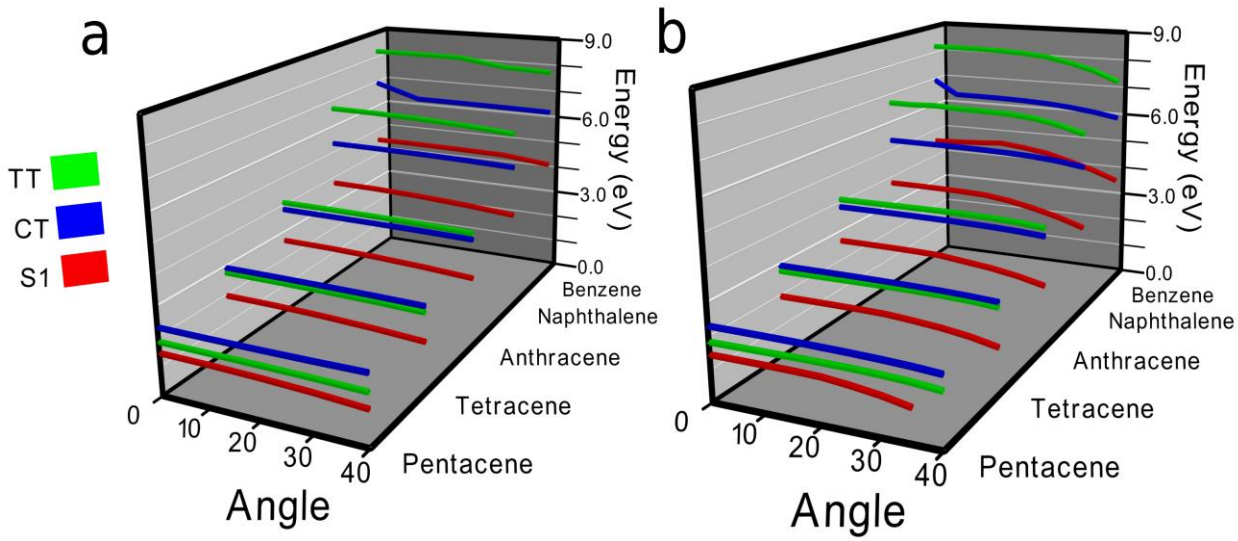

Figure S-3 Dependence of S_1, CT, and TT excitation energy on (a) the herringbone angle θ (b) the angle ϕ between the acene dimer and the COF plane, for all investigated acene-COFs.

5. Optimized Cartesian coordinates of acene-COF structures

The structures provided here are unit cells of each SCC-DFTB-optimized acene-COF monolayer. Optimized structures of two-layer acene-COF unit cells in the four stacking orientations described in the manuscript (AA, serrated AA, inclined AA, and AB) are available in the DFTB+ `.gen` file format within the `.zip` archive accompanying this Supporting Information.

```
120
Benzene-COF monolayer: a=b=36.69, c=100.00
    H     15.09141133     12.65723206      2.18517751
    C     16.01745169     13.25955954      2.15567743
    O     13.38716898     14.77387699      2.13878206
    B     14.63184378     15.39699873      2.10170564
    C     11.05176410     15.76897217      2.15241766
    C     12.44727290     15.84229877      2.12398540
    C     17.23777621     12.59984728      2.16644679
    C     19.17415858      1.32064706      2.17596152
    H     17.25551105     11.49339818      2.20314273
    H     18.57205647      6.41671641      2.20471403
    C     15.93895267     14.66759987      2.10876297
    H     10.50254256     14.81485115      2.18967707
    H     18.07321705      1.33277025      2.21030499
    C     19.56876320      6.89183083      2.15992203
    H     18.70965692      8.87027956      2.21632240
    O     19.50569650      3.84015297      2.14776368
    C     13.14608191     17.05835572      2.07781821
    C     19.94623136      2.48586380      2.14318930
    C     19.64384403      8.27755210      2.16705692
    O     14.54097472     16.78577335      2.06211194
    B     20.67641198      4.59287593      2.10525116
    C     12.51002127     18.30222019      2.05701688
    C     18.45571589     13.30421892      2.13240171
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    C     21.34858642      2.46845740      2.09898635
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    C     19.74911645     11.17193009      2.12907957
    C     22.09682777      1.28892280      2.08632225
    C     18.38717238     14.70856860      2.08526963
    H     18.77942792     10.63543436      2.11400052
    C     19.74286863     12.57429388      2.14268385
    C     20.88071528      8.94735186      2.11648691
    O     21.82480119      3.80647667      2.07327972
    C     20.93669215     10.42594738      2.13208816
    H     13.05928505     19.25631844      2.02221741
    H     17.15957301     16.47043859      2.03426473
    C     21.96260556      6.76891368      2.04467682
    C     20.98077350     13.23660320      2.16554513
    C     22.04138096      8.15483448      2.05255423
    H     23.19751419      1.27761212      2.05283392
    C     22.15274180     11.12820026      2.15371948
    H     19.31698955     15.30548499      2.05532871
    C     22.19638897     12.53228709      2.17359553
```

H	21.00424585	14.34311892	2.18000598
H	22.90098992	6.18731697	1.99344452
H	23.10420829	10.56222626	2.15882046
H	23.03597701	8.63556754	2.00743719
C	23.49013175	13.25449990	2.20405810
C	23.54454681	14.66085937	2.23177762
H	22.60342873	15.24190047	2.23047412
C	24.71705123	12.56486259	2.20802448
C	24.75666884	15.33674269	2.26040525
H	24.71867059	11.45904873	2.18742911
C	25.92775339	13.24375028	2.23659398
H	24.74143504	16.44163889	2.28101756
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H	26.86077063	12.65158792	2.23766941
O	27.39624436	16.77839738	2.30842626
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C	29.48713010	15.82442187	2.30763509
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C	30.88350794	15.74331337	2.31092109
C	30.83682975	18.20334470	2.33856671
O	31.78182453	19.26771759	2.34774061
C	31.53004360	16.98350677	2.32646343
B	33.02659342	18.64194752	2.33874322
C	34.37522806	20.79900908	2.33344580
C	38.14687972	25.92011679	2.18783132
C	38.16140751	27.30789384	2.17452611
C	35.57690939	21.49568828	2.31392767
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C	41.88815316	19.43471999	2.19608736
C	43.09520758	18.75010803	2.17537662
C	36.81528852	20.82575084	2.29162996
O	32.92880435	17.25201454	2.32779732
C	38.12576131	22.97320686	2.24750031
C	40.53303748	22.97508155	2.19650906
H	37.17633887	25.39063457	2.18860431
C	38.10003193	21.56848285	2.26160921
C	39.32955677	23.69670887	2.21516368
C	39.34093510	25.17679751	2.19979091
C	35.57219430	18.72493290	2.31422834
C	39.33030443	20.89039488	2.24193413
C	40.55817003	21.57207021	2.20875052
B	39.37595938	29.53740867	2.15828075
H	37.19559483	27.84479040	2.16465314
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H	33.43443261	21.37846076	2.34852109
C	36.77613528	19.41802898	2.29491906
O	45.71848224	17.28910751	2.15543447
C	39.36732045	28.04040264	2.17119381
C	41.84465059	20.84067427	2.18578608
H	40.94307190	18.86128794	2.22168464
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    C     44.28120798     20.83551675      2.13073676
    H     37.16741474     23.52747220      2.26191609
    C     40.09425603     31.64649092      2.12004232
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    H     39.33272708     19.78334909      2.25199758
    O     40.54162487     30.29767400      2.11860119
    H     35.60366723     17.62035399      2.31353784
    H     37.72313864     18.84683395      2.27959128
    H     41.53788450     27.80466750      2.18025305
    H     41.51044365     25.35151172      2.20503854
    H     45.21947721     21.41934095      2.10529072
    H     43.08527989     22.62925026      2.14303047
    H     28.89849770     19.24392621      2.34430593
    H     31.42742966     14.78503239      2.29989935

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Naphthalene-COF monolayer: a=b=40.88, c=100.0
    H     14.33713291     12.44953703      2.25759211
    C     15.27726947     13.03021759      2.25493642
    O     12.67981521     14.55179259      2.23028368
    B     13.92331297     15.18131558      2.21412314
    C     10.35783090     15.56121452      2.22765451
    C     11.73349755     15.61610520      2.21524129
    C     16.48178983     12.34055559      2.27563631
    C     18.64526976      1.00272365      2.29659613
    H     16.46602091     11.23388291      2.29380521
    H     17.96114527      6.04024707      2.30557747
    C     15.22465634     14.44070980      2.23093418
    H      9.82132193     14.59814603      2.24989334
    H     17.54309888      1.01869638      2.32248143
    C     18.94220990      6.54808926      2.28750081
    H     18.01182366      8.49177042      2.32863083
    O     18.93295161      3.52128424      2.27598504
    C     12.43219744     16.84197190      2.18818593
    C     19.37941310      2.16759939      2.27123305
    C     18.96891711      7.93611570      2.30083165
    O     13.83042318     16.57135595      2.18625601
    B     20.10135200      4.28106367      2.24830931
    C     11.77970743     18.05381739      2.17197861
    C     17.71703683     13.01686174      2.27520937
    C     16.46680507     15.11074772      2.22892521
    C     20.79024756      2.15800665      2.23897024
    C     20.12545989      5.77868998      2.25330540
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H	20.24986942	14.04936485	2.34406432
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C	22.81460904	14.38327121	2.41294344
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O	27.81365747	14.49801487	2.48204522
C	28.05676095	16.78902413	2.50612645
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C	30.13503798	15.51473579	2.51437174
C	30.13532128	18.00462236	2.53440349
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C	30.85720894	16.74834509	2.53032152
H	30.31571346	20.19985375	2.54978087
C	32.23093932	19.18857004	2.55475878
O	33.17081551	20.25694048	2.56214567
C	32.28652875	16.75120161	2.53926959
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C	35.71011307	20.38686060	2.54872091
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C	39.47904867	23.99348446	2.44147255
C	41.88404692	24.00301700	2.35299561
H	38.50496433	26.36732215	2.41951624
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C	40.67924224	24.72003687	2.39451267
C	49.09554977	16.79095167	2.23388381
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C	41.91335593	22.60076590	2.35716886
B	40.63948184	30.55872343	2.33984537
H	38.47386827	28.82353406	2.39712749
B	46.95896235	19.66580612	2.23213011
H	34.79488493	22.36548895	2.56933644
C	38.15518722	20.43502715	2.49603047
O	47.04794664	18.27552267	2.24672668
C	40.64201077	29.06187659	2.36004486
C	43.19648838	21.86291585	2.31608606
H	42.26377253	19.89938935	2.34355492
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H	44.37875662	18.65059711	2.29069828
C	45.66259504	20.41375958	2.25385877
H	36.90367353	23.61020900	2.52040811
C	50.52396556	16.79255181	2.21486468
H	32.84653905	15.80139405	2.53494162
C	39.94169207	32.67780940	2.32345568
H	48.53717188	15.84025595	2.25662425
C	39.21552160	33.84729241	2.32334922
C	41.86774238	26.94344784	2.36157451
H	42.83918107	24.56094088	2.31500538
C	41.84946616	28.33099506	2.34923153
C	49.14466308	19.22922443	2.19887305
C	44.43541173	22.53083193	2.27944531
C	45.63003478	21.82446618	2.24946893
H	38.52230887	24.54840420	2.47421460
C	51.24246378	18.05102135	2.18653532
C	41.35264870	32.67120630	2.29254424
O	48.20139464	20.29465325	2.20147144
H	40.69614840	20.80881883	2.40726255
C	50.51946510	19.28332446	2.17763069
O	41.80453750	31.32149914	2.30295517
C	39.92936366	35.08461728	2.29232562
H	38.11272560	33.83752481	2.34826822
H	36.99873947	18.62726026	2.52418654
H	39.10838100	19.87444489	2.47417206
C	42.08538664	33.83562885	2.25964948
C	41.37857268	35.07770658	2.25976653
H	42.81286753	28.87074200	2.32985194
H	42.84092771	26.41728393	2.35128738

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    H     46.57768982     22.39130541      2.22374809
    H     44.46567911     23.63653430      2.27633865
    H     51.05594931     20.24649697      2.15703010
    H     43.18771185     33.81896896      2.23566109
    H     28.14756577     18.95356741      2.52472973
    H     30.67524123     14.55323104      2.51058276

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Anthracene-COF monolayer: a=b=45.18, c=100.00
    H     18.74894857     14.84635432      2.28046298
    C     19.68190276     15.43916437      2.27596070
    O     17.06602925     16.95625162      2.24156195
    B     18.31076998     17.58290349      2.22752214
    C     22.98357528      0.98453966      2.29138990
    C     14.74948971     17.96649270      2.23112605
    C     16.11989612     18.02147085      2.22194652
    C     20.89454229     14.76446732      2.29697927
    C     22.96503436      3.46750502      2.27870354
    H     20.89564850     13.65792791      2.31702507
    H     22.32065254      8.51278754      2.30981567
    C     19.61529544     16.84858326      2.24851215
    H     14.21007702     17.00463758      2.25399457
    H     21.86288584      3.49277980      2.31513293
    C     23.30821259      9.00790734      2.28729278
    C     23.66659783      2.21267872      2.26154902
    H     22.40514261     10.96446865      2.34117944
    C     14.02615715     19.20847977      2.21513117
    O     23.27302142      5.97657248      2.26671791
    C     12.62126895     19.24257012      2.23153496
    C     16.82711959     19.25112437      2.19403580
    C     23.70872556      4.61977684      2.25192847
    C     23.35317491     10.39501315      2.30536781
    O     18.22290288     18.97306999      2.19626051
    B     24.44551624      6.72912979      2.23143661
    C     14.74998514     20.46494242      2.18623313
    C     16.18624645     20.46323895      2.17400224
    C     22.12179807     15.45416638      2.29321418
    C     25.11604816      2.19804191      2.21530670
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192
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H	26.45250283	12.94180196	2.32623392
H	26.42265248	11.09377094	2.21035395
C	26.84530819	15.63805031	2.37762321
C	26.89263558	17.04437053	2.39819494
H	25.94875559	17.62118264	2.39925353
C	28.07399762	14.95169643	2.37821438
C	28.10100923	17.72594614	2.41529481
H	28.08317829	13.84563463	2.36317423
C	29.28149783	15.63611505	2.39560509
H	28.08347538	18.83092687	2.42963754
C	29.33734228	17.04596002	2.41338702
B	30.63847216	17.78610876	2.42518317
H	30.21917689	15.05088208	2.39388459
O	30.72465870	19.17644511	2.43541402
O	31.88156136	17.15740281	2.42376956
C	32.12018995	19.45529051	2.43997535
C	32.82830304	18.22105239	2.43300914
C	32.75795195	20.66528785	2.44859968
H	32.19669982	21.61452156	2.45351796
C	34.19509935	18.16081585	2.43476691
C	34.19930118	20.66899598	2.45061331
C	34.92168325	21.86294168	2.45860704
C	34.92640280	19.40340907	2.44374264
C	36.33857496	21.89426903	2.45988625
H	34.73034164	17.19653853	2.42910833
C	37.06463479	23.09929204	2.46672972

C	36.32211512	19.42681121	2.44547513
C	37.06299442	20.63550556	2.45310235
C	42.69651875	25.54781899	2.45988759
O	43.63598740	26.61600914	2.45558971
C	38.47019384	20.65887834	2.45341309
C	43.41046859	24.31688042	2.45209696
B	44.88344272	25.99581103	2.44376281
C	46.18126087	28.17341678	2.43078195
C	49.77826050	33.33375259	2.34042737
C	49.71490705	34.71995742	2.32882213
C	47.36517252	28.89722870	2.41096521
C	46.16925122	26.76191509	2.42909555
C	53.64758915	26.93522345	2.26790734
C	54.84158340	26.22917676	2.24162900
C	48.61541626	28.25169733	2.38784792
O	44.80570564	24.60465815	2.44248638
C	49.87685646	30.42449974	2.36086430
C	52.28452217	30.48055587	2.30933716
H	48.83846581	32.74981256	2.35821550
C	49.88058493	29.02118883	2.36241262
C	51.06323431	31.17386019	2.33409685
C	59.49340168	23.24026518	2.16768573
C	51.01062451	32.65359374	2.32798919
C	47.42732464	26.12321799	2.40786352
C	51.12411640	28.37091849	2.33617813
C	52.33789273	29.07690339	2.30943040
B	50.82755153	37.01017100	2.28190221
H	48.72061397	35.20205713	2.33770041
B	57.38141487	26.12771763	2.20152687
H	45.22485174	28.72705893	2.44754575
C	48.61332062	26.84430021	2.38776222
O	57.46194279	24.73680643	2.19749794
C	50.88030947	35.51426282	2.30333580
C	53.62458924	28.34268403	2.28076424
H	52.69120427	26.37884053	2.27914310
C	58.85740770	24.45177716	2.17657345
O	49.64906129	37.75353647	2.30440571
H	54.80181066	25.12465874	2.23254982
C	56.09030546	26.88536457	2.22646405
H	47.32128649	30.00273671	2.41231086
C	60.93558360	23.23341095	2.15040814
C	50.07427203	39.11383506	2.26678216
H	58.93003138	22.29164041	2.17579849
C	49.32360385	40.25831391	2.26905919
C	52.17809014	33.43861890	2.30593956
H	53.23026781	31.05566472	2.28747953
C	52.11191658	34.82494787	2.29360777
C	59.56839680	25.68442229	2.16740464
C	54.86592973	29.00559108	2.26504386
C	56.05941456	28.29635231	2.23875780
H	48.90676690	30.95954402	2.38015061
C	61.66301709	24.49902751	2.14098509
C	51.49643428	39.13829949	2.22239362

O	58.62698107	26.75077266	2.18278670
H	51.15104411	27.26313311	2.33576031
C	60.93472168	25.74251171	2.14887957
O	51.97434004	37.79911701	2.23297849
C	50.01485228	41.52442823	2.22507118
H	48.22139176	40.22586721	2.30412328
H	47.48056915	25.01927097	2.40585232
H	49.57548114	26.29898861	2.37030835
C	52.20846566	40.30508340	2.17772914
C	51.47360159	41.54489713	2.17854428
H	53.05823519	35.39525052	2.27530698
H	53.16825834	32.94543879	2.29676874
H	57.00846130	28.86282386	2.22798502
H	54.89860045	30.11100737	2.27425598
H	61.47255250	26.70523002	2.14257806
H	53.31074544	40.30755938	2.14302201
H	26.70888819	1.22493040	2.06491149
H	21.69223881	1.20648651	2.21407676
H	14.32111352	22.98487899	2.13373606
H	11.83917456	18.62212606	2.15733534
H	36.87173026	18.46862407	2.44011022
H	34.37071929	22.82037814	2.46353650
C	39.19695627	21.86419035	2.45897192
C	38.47130273	23.12230310	2.46596520
H	36.51388601	24.05709978	2.47178028
H	39.02143547	19.70131443	2.44805219
C	40.61440233	21.89868237	2.45651837
C	39.20891365	24.33232468	2.47045084
C	52.13137558	42.77415504	2.13745951
C	51.43579732	44.00846919	2.14255118
C	49.98416401	43.99321562	2.18837738
C	49.32307586	42.73794537	2.22690953
H	53.23540784	42.78867043	2.10244710
H	48.21915681	42.72053164	2.26224586
C	63.05801276	24.47708324	2.12774920
C	61.65896706	22.03962205	2.14531710
C	63.79870884	23.26928715	2.12717183
C	63.07664311	22.00912617	2.13580355
H	61.10654782	21.08298183	2.15267224
H	63.60809351	25.43509682	2.12126105
C	41.33480536	23.09435031	2.45898113
H	41.16802127	20.94267055	2.45088644
C	40.60397692	24.35816348	2.46645115
H	38.65780460	25.28970109	2.47576268
C	42.77697084	23.10409864	2.45228848
C	41.32990351	25.60338486	2.46759368
H	43.34239563	22.15689979	2.44574268
H	40.79143628	26.56616219	2.47275472
C	52.10679369	45.24410951	2.10841658
C	51.41529446	46.46926721	2.12140710
C	49.96357989	46.45884474	2.16565768
C	49.29250143	45.22057855	2.19585304
H	48.18776970	45.21283865	2.23035780

H	53.21157213	45.24976409	2.07452091
C	65.21511738	20.78883706	2.13927269
C	65.93641940	22.04943410	2.13181818
C	65.20559406	23.25160127	2.12299806
C	63.80771178	20.80660618	2.13863774
H	63.25976471	19.84731257	2.14515413
H	65.75202392	24.21216448	2.11734181

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