Molecular asphaltene models based on Clar sextet theory

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SUPPLEMENTARY INFORMATION

Clar's theory of the aromatic sextet

Initially developed in 1972, Clar's theory of the aromatic sextet[1,2,3] represents the delocalization of six π-electrons in a single benzene-like ring with a circle inscribed in the hexagon, which denotes a "Clar sextet" (See Figure s1a). Consequently, two adjacent rings cannot host a circle at the same time, since it would mean 12 π-electrons for just 10 carbon atoms. Furthermore, according to this theory the structure with largest number of π-sextets is the most stable among all possible configurations. Based on these simple statements, Clar's theory of the aromatic sextet predicts the aromaticity distribution of PAHs and explains the stability and many of their chemical properties.[4,5,6,7,8] For instance, in the case of phenanthrene (Figure s1b) the resonance structure with two Clar sextets is more representative than the one with a single inscribed circle, and therefore outer rings have larger local aromaticity than the central one.[9,10,11] On the other hand, anthracene shows three equivalent Clar configurations and therefore the resulting structure is a superposition of the three, with similar aromaticity for the three rings.[9,10,11] As a general idea, a PAH with a given number of aromatic π-sextets is kinetically more stable than its isomers with less aromatic π-sextets.[1,2,3,12] Therefore, the higher the numbers of circles we draw in the structure, the more stable the molecule would be (see isomers in Figure s1d).[13] Further information can be found in a recent review by Solà.[3] This theory has been even proved useful in the study of many novel nano-structures such as carbon nanotubes,[14,15,16,17] graphene nanoribbons,[18,19,20,21] carbon nanocones,[22] and carbon nanotori.[19]
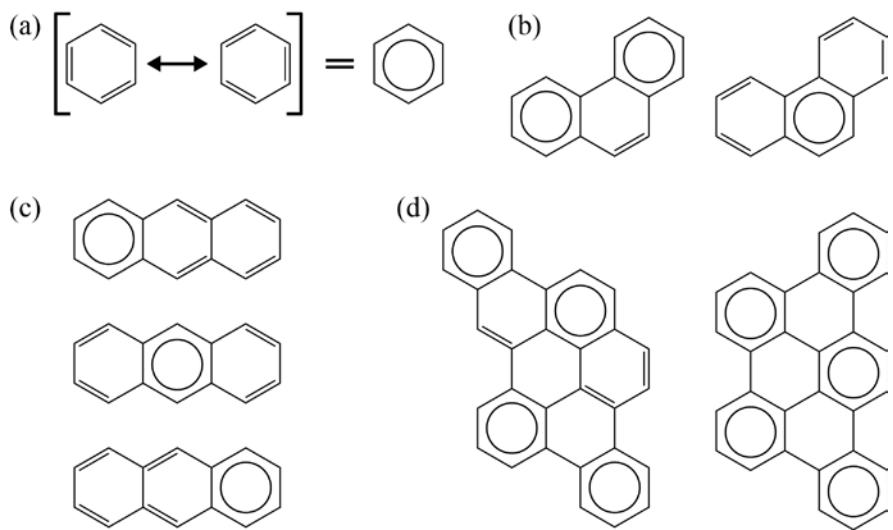
Figure s1. (a) Clar sextet representation of the delocalization of six π-electrons resulting from the resonance of two Kekulé bond configurations with alternating single and double bonds. (b) Phenanthrene Clar structures with two and one Clar sextets respectively. (c) Anthracene equivalent Clar configurations that result in a final structure superposition of the three. (d) Clar structure of benzo [*qr*] naphto [2,1,8,7-*fghi*] pentacene (left) and tribenzo [*fg, ij, rst*] pentaphene (right).

PAH representative of the FAR region of asphaltenes

Aiming to reduce the size of the model systems for DFT calculations, we consider smaller PAHs that contain the same FAR region. These PAHs retain the same electronic distribution and geometrical effects in the aromatic system, but with considerably smaller number of atoms. Three different molecular structures for representing A1 are investigated.

The planarity of the aromatic structure is studied using the Cremer-Pople pucker amplitude.[23] This method provides a general quantification of the ring deformation by introducing ring-puckering coordinates that can be applied without approximation to any cyclic molecule, given only the coordinates of the nuclear positions of the atoms in the ring. It is also independent on the number and type of atoms and the size of the ring. The coloring is done with the color scale provided by the PaperChain representation in VMD,[24] where Cremer-Pople pucker amplitude is calculated and color-coded,[25,26] using Hill-Reilly method.[27] In this coordinate system the radius Q means the magnitude of puckering, measuring the deviation from the perfectly flat six-membered ring ($Q = 0$). In this scale, red rings are planar, green rings are highly deformed and the orange-colored ones are partially deformed. This representation allows us to study the deformation in the polyaromatic core of the molecules under study.

Figure s2 depicts the fully optimized geometries of these molecules, where the rings are color-coded following the Cremer-Pople pucker amplitude, as implemented in VMD molecular visualization. The values of Q are shown inside the hexagons. These color-coding allow us to quickly visualize qualitatively the deformation of the rings with respect to planarity. Red rings are those completely planar while green ones are the most deformed and the values closer to zero. The first model is the most simplified one, where hydrogen atoms saturate all terminal carbons in the structure (Figure s2a). In the second model, methane groups saturate those positions where aliphatic chains should be in the complete molecule (Figure s2b). The third model shows the complete structure where all aliphatic chains are included (Figure s2c). Remarkably, pentane effect does not depend on the aliphatic chains, but the strain that undergoes the polycyclic aromatic core remains in the three molecules independently on the edge configuration, as it is clearly noticed by the same colors for the Cremer-Pople pucker amplitude. Obviously, the higher deformation takes place in the cyclohexane ring, which is not aromatic at all, while the polycyclic aromatic system goes from orange (partially deformed) to red (planar).
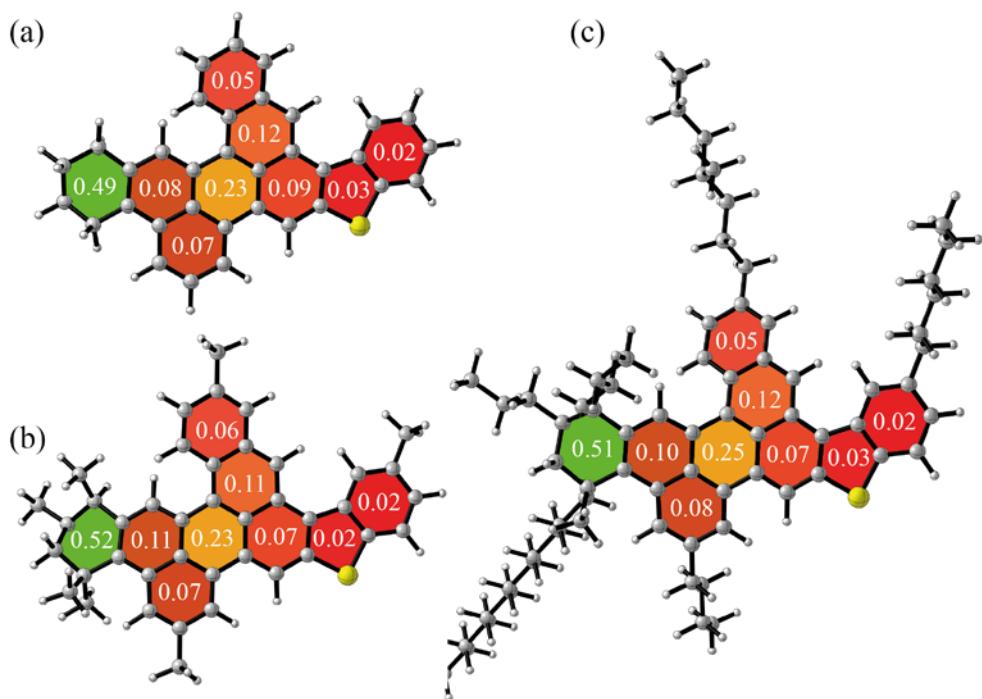
Figure s2. Different models for A1 molecule color-coded with pucker Cremer and Pople amplitude. The values of Q are shown inside the hexagons. (a) Simplified model with hydrogen atoms saturating all carbon atoms. (b) Model with methane groups saturating positions of aliphatic chains. (c) Complete molecular structure.

Supplemental references

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XYZ Coordinates

A1-M1

C	3.546834	-3.018454	-0.711903
C	2.456754	-3.768657	-1.111959
C	1.157611	-3.242864	-1.029255
C	0.942358	-1.937396	-0.591036
C	2.069869	-1.115078	-0.294699
C	3.387516	-1.679492	-0.265338
C	4.493588	-0.901389	0.223296
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C	2.966016	0.962708	0.531470
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C	-0.577906	0.037155	-0.197618
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A1-M2

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A2-M1

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C	1.652497	-3.137949	-0.569709
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H	-5.869440	1.613304	1.341949
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C	-1.693388	4.628295	-1.128090
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H	-0.403434	6.377450	-1.160843
H	1.585792	5.148899	-0.456107
H	-2.707874	2.766601	-1.042533

A2-M2

C	-4.796256	1.625016	-0.198774
C	-3.655756	0.791436	-0.056555
C	-2.318299	1.365667	-0.016373
C	-2.157881	2.778295	0.072769
C	-1.183074	0.521493	-0.000403
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C	0.268058	2.503102	0.051345
C	0.130551	1.087814	0.022787
C	1.298081	0.252202	0.008913
C	2.598757	0.859086	0.019899
C	2.691573	2.287149	0.045568
C	1.576195	3.074269	0.060952
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H	3.669110	2.752505	0.054147
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C	-3.820146	-0.609412	0.052381

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C	-0.196729	-1.761465	-0.024862
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C	-6.061680	1.059876	-0.119930
C	-6.222914	-0.317085	0.106005
C	3.745115	0.022302	0.003348
C	3.554318	-1.378447	-0.021783
H	-6.939594	1.693870	-0.227568
H	-7.223522	-0.732007	0.210549
H	0.435832	-3.831587	-0.072342
H	2.228042	-3.059595	-0.050711
C	-4.592958	3.091486	-0.505110
H	-4.429647	3.209657	-1.588259
H	-5.496233	3.662495	-0.259896
C	-3.381872	3.651649	0.244741
H	-3.623451	3.707729	1.318318
H	-3.165180	4.675967	-0.080874
C	5.183775	0.243481	0.005550
C	5.790880	-1.046651	-0.018073
C	6.028798	1.367963	0.024488
C	7.411702	1.194113	0.019705
H	8.059401	2.066486	0.034348
C	7.981235	-0.091946	-0.003900
H	9.062442	-0.202038	-0.007249
C	7.175881	-1.229017	-0.023072
H	5.625969	2.374302	0.042718
H	7.611082	-2.225266	-0.041424
C	-5.260784	-2.630796	0.501450
H	-5.135444	-2.775557	1.586545
H	-6.269107	-2.981984	0.252506
C	-4.205127	-3.458240	-0.235218
H	-4.450674	-3.477970	-1.309615
H	-4.223294	-4.499892	0.107181
N	4.790375	-2.002344	-0.033917
H	4.937698	-3.000190	-0.052178

A2-M3

C	-5.006821	-1.111754	0.205326
C	-3.745802	-0.475999	0.059939
C	-2.520634	-1.261353	0.017829
C	-2.592031	-2.681169	-0.071043
C	-1.263076	-0.613770	-0.001537
C	-1.428124	-3.421631	-0.092021
C	-0.154109	-2.810569	-0.054191

C	-0.062101	-1.390114	-0.026448
C	1.223518	-0.753116	-0.015550
C	2.396869	-1.573207	-0.028287
C	2.270574	-2.997401	-0.052304
C	1.042704	-3.593275	-0.065163
H	-1.483133	-4.507399	-0.154762
H	3.165619	-3.615280	-0.061479
H	0.956258	-4.677227	-0.085819
C	-3.678012	0.932843	-0.049568
C	-2.381359	1.600328	-0.018737
C	-4.872445	1.686574	-0.184607
C	-1.182854	0.828531	-0.005274
C	-2.319108	3.007244	0.067102
C	0.086905	1.477966	0.018345
C	-1.070036	3.624857	0.089638
C	1.321355	0.680291	0.008937
C	0.105802	2.880783	0.050185
H	-1.011909	4.710098	0.147687
C	2.587801	1.272897	0.022126
C	-6.162855	-0.347223	0.129417
C	-6.096671	1.037442	-0.097693
C	3.643646	-0.916246	-0.014715
C	3.747740	0.490822	0.010027
H	-7.132450	-0.828775	0.240359
H	-7.015962	1.610693	-0.200475
H	1.048341	3.416503	0.060037
H	2.692519	2.351915	0.040335
C	-5.044494	-2.591581	0.512665
H	-4.899470	-2.734065	1.595480
H	-6.029224	-3.008119	0.270094
C	-3.942974	-3.342100	-0.239934
H	-4.192280	-3.356388	-1.313113
H	-3.896263	-4.388473	0.084292
C	5.857486	-0.429413	-0.003143
C	-4.770203	3.161974	-0.499341
H	-4.624766	3.282355	-1.584927
H	-5.707301	3.673323	-0.249478
C	-3.592079	3.807364	0.233415
H	-3.829018	3.870203	1.308101
H	-3.441168	4.837037	-0.112402
C	5.163262	0.809663	0.017363
C	5.895429	2.004325	0.038776
C	7.288374	1.946606	0.039212
H	7.866337	2.866566	0.055696
C	7.957792	0.707882	0.018565
H	9.044464	0.687089	0.019267
C	7.253245	-0.496022	-0.002835
H	7.775210	-1.449650	-0.018807
H	5.385863	2.964666	0.054884
N	4.920576	-1.454600	-0.022034
H	5.144018	-2.437555	-0.039592

A3-M1

C	4.018968	-1.594650	-0.011890
C	3.645095	-0.226064	0.002626
C	2.256260	0.136909	0.002057
C	1.265902	-0.900226	-0.011719
C	1.680666	-2.225638	-0.031693
C	3.046154	-2.570516	-0.030076
C	1.885402	1.519414	0.012886
C	-0.164346	-0.530423	-0.007328
C	-0.541070	0.852029	-0.008367
C	0.452565	1.885088	0.008661
C	-1.936908	1.196495	-0.016194
C	-2.942863	0.170815	-0.035041
C	-2.547374	-1.159168	-0.001017
C	-1.171901	-1.481669	0.009730
H	5.075712	-1.857443	-0.010749
C	4.630717	0.794795	0.017070
C	4.256521	2.121005	0.028205
C	2.895614	2.479355	0.025381
H	5.681378	0.514097	0.018141
H	5.012199	2.902460	0.038440
C	0.035558	3.213598	0.025541
C	-2.294045	2.571517	0.006295
H	-3.339228	2.858718	0.014686
C	-1.326397	3.554072	0.027773
H	-1.615009	4.602052	0.047567
C	-5.358293	-0.622434	-0.361108
H	-5.325272	-0.857668	-1.435028
H	-6.390588	-0.327029	-0.135187
C	-4.954327	-1.865864	0.434046
H	-4.970606	-1.636345	1.509598
H	-5.666607	-2.684519	0.271613
C	-4.414567	0.551767	-0.061983
H	-4.687571	0.996154	0.908568
H	-4.581365	1.340026	-0.806882
C	-3.546933	-2.304214	0.018609
H	-3.592169	-2.756626	-0.984801
H	-3.177314	-3.093499	0.686478
H	0.761783	4.018171	0.040963
H	2.650769	3.535231	0.032486
H	-0.918502	-2.537123	0.034746
H	0.973059	-3.045723	-0.050345
O	3.325156	-3.914702	-0.048364
H	4.285697	-4.049274	-0.048186

A3-M2

C	4.163093	-1.890304	-0.012748
C	3.806142	-0.552291	-0.004166
C	2.458603	-0.131398	-0.001345
C	1.445962	-1.130091	-0.007991

C	1.823376	-2.488518	-0.019920
C	3.156222	-2.867807	-0.021132
C	2.093586	1.289302	0.008482
C	0.030883	-0.734808	-0.006678
C	-0.315975	0.648119	-0.009884
C	0.712706	1.654187	0.003556
C	-1.696050	1.029069	-0.018911
C	-2.721523	0.043113	-0.036744
C	-2.361201	-1.309324	-0.006284
C	-1.006290	-1.668680	0.007010
H	5.213229	-2.177495	-0.014541
C	3.052847	2.312817	0.022697
C	0.349977	3.036737	0.016157
C	-2.011579	2.432980	0.001394
H	-3.050331	2.743358	0.011049
C	-1.039179	3.386483	0.018599
H	-1.306649	4.440885	0.036297
C	-5.162346	-0.685955	-0.353956
H	-5.141489	-0.918132	-1.428895
H	-6.184757	-0.362322	-0.121736
C	-4.789034	-1.943186	0.434166
H	-4.789244	-1.717356	1.510685
H	-5.526406	-2.740006	0.274946
C	-4.185319	0.460666	-0.054502
H	-4.441706	0.903684	0.921023
H	-4.337615	1.257668	-0.792718
C	-3.399364	-2.420720	0.002719
H	-3.469040	-2.852393	-1.008292
H	-3.051883	-3.233806	0.653231
H	-0.779028	-2.729632	0.031192
H	1.084191	-3.279938	-0.030518
O	3.434716	-4.212025	-0.032055
H	4.394596	-4.348976	-0.034663
C	1.350384	4.026300	0.029991
C	2.689152	3.662868	0.032641
H	4.109909	2.071801	0.027151
H	4.604128	0.181242	0.000148
H	3.463459	4.425759	0.043608
H	1.060477	5.074509	0.039571

Frequencies (cm^{-1})

A1-M1

24.5671	38.6979	51.9766
67.6140	89.6187	96.0661
107.7388	116.6438	136.6189
158.4289	183.1262	198.3353
203.6983	218.5812	241.7772
258.5102	281.0699	289.0628
302.4864	309.2849	328.7730

335.7608	366.3370	380.8825
399.9003	417.0064	435.3845
441.5854	456.4529	481.4269
494.4209	498.9913	502.1995
507.3865	526.4699	532.3123
546.3781	557.8105	566.9750
574.1096	585.0122	618.5073
629.0046	642.8337	646.1709
663.1018	677.6096	683.2225
690.3780	715.0823	722.7728
732.9839	748.2963	755.6517
763.7307	771.0302	776.7547
782.1841	801.6162	822.0683
830.8523	843.6574	847.4743
858.6300	861.0897	875.5833
885.2265	887.9638	902.7055
916.4272	920.2551	931.0840
937.0615	944.8407	952.2878
970.5492	972.7760	975.9028
983.8354	990.1792	1002.4512
053.7193	1056.3051	1061.8269
076.7414	1086.5385	1095.7928
111.5746	1115.1106	1127.8080
164.7629	1169.8080	1175.2127
186.6158	1194.9592	1195.5458
205.3186	1209.1410	1230.7002
239.4664	1244.7058	1251.3558
275.1969	1287.6127	1293.2449
304.2254	1319.4917	1327.0190
339.1850	1343.9255	1354.1868
368.5000	1376.7826	1386.8413
390.5019	1391.9480	1399.7386
405.9339	1410.8651	1415.2148
426.5438	1442.0642	1461.5729
473.6499	1482.2069	1499.8345
501.0097	1506.9203	1512.3618
520.4815	1522.0032	1532.1766
545.5658	1567.7513	1581.0184
602.0338	1605.9251	1622.5545
629.7980	1632.8733	1642.1974
651.3830	1669.2159	3001.9093
006.7740	3024.4034	3030.7283
061.3955	3066.2771	3075.3921
078.7857	3176.1450	3185.9397
186.5269	3187.5372	3195.3376
203.5186	3206.3947	3209.1868
209.9392	3219.9405	3223.8435
237.1081	3246.9784	3281.4353

A1-M2

23.6556	38.5612	57.3169

76.1787	89.6030	90.5664
101.6510	122.8140	149.2273
166.2468	180.4255	190.7135
209.2542	219.4774	239.8501
245.7804	270.7617	281.7589
291.0332	310.3039	322.9619
348.3240	351.4169	389.0814
400.3797	416.4277	443.2329
445.8264	466.1221	473.4621
491.9342	494.3303	504.1281
505.4476	523.5207	530.6063
537.9330	551.9095	573.4488
583.0404	598.2223	626.6483
635.6456	638.8749	651.7369
659.7008	670.5094	688.1400
693.1331	704.8536	724.2723
741.8884	747.5458	758.8310
763.6247	771.8998	772.8638
782.9100	798.8768	819.2659
823.0764	845.5296	858.5316
860.4603	864.0347	870.5282
882.4361	885.5170	896.6745
898.1300	901.0826	932.0739
937.6564	943.4034	946.2112
962.5048	966.8380	979.0735
985.0641	994.1248	1022.1131
1054.8899	1062.7857	1064.3681
1084.6641	1089.6024	1096.8616
1108.1099	1113.3254	1133.8010
1163.2103	1169.0212	1179.4419
1184.6686	1190.0416	1193.1340
1200.3477	1209.4385	1220.6248
1237.6409	1250.8840	1259.1271
1282.9967	1286.9170	1292.7401
1302.3533	1315.2793	1320.0189
1338.1183	1342.9703	1349.4923
1358.4692	1370.6067	1376.6464
1388.1934	1389.9302	1391.3254
1403.8039	1411.1133	1415.5479
1430.4046	1448.7127	1459.0884
1482.2039	1485.7191	1499.1293
1501.6949	1508.4110	1514.3414
1521.0929	1528.9554	1533.0001
1544.1194	1562.3094	1584.0603
1606.1658	1610.8443	1622.8300
1635.2906	1640.6085	1647.1992
1656.3377	1661.1254	3011.4616
3015.5370	3033.8213	3040.0076
3070.6210	3072.0920	3085.2035
3088.5146	3184.2481	3193.7180
3194.8492	3196.3792	3197.4135
3203.8136	3211.9357	3216.5248

3218.9459   3219.3677   3233.5065
3237.6205   3241.3513   3245.9070

<u>A1-M3</u>

16.6176   35.2922   47.6586
48.9772   59.6258   77.4924
94.8485   111.9579   121.3069
151.3534   161.2399   188.2748
189.1035   222.8359   235.1981
243.3543   265.8443   287.3585
292.5593   299.6533   307.2610
334.5289   347.3011   371.7246
406.1454   427.6616   439.5890
451.6848   459.0644   469.2679
498.9678   507.1527   513.8415
517.0993   522.7939   537.8176
540.9102   565.0876   587.0661
589.4470   598.0881   612.0262
627.5331   634.3702   654.7164
665.1255   674.6900   683.3208
697.5464   730.3423   735.4074
740.8117   749.8610   756.0435
761.3861   766.5958   771.5098
772.8799   791.9642   799.2867
820.2552   831.8216   846.8680
856.2793   864.5991   868.8629
874.4084   887.8355   890.8880
898.4684   904.1070   927.1891
934.6848   939.0764   941.0794
957.6173   961.0865   964.7154
976.6421   980.0162   1011.3351
1051.9365   1066.1897   1076.5995
1083.7643   1089.8573   1098.1888
1103.1714   1113.3764   1141.8720
1156.0250   1175.2360   1182.7458
1183.1380   1193.1574   1195.6629
1209.1083   1217.8510   1224.7164
1232.2319   1245.0630   1262.5223
1271.2831   1284.1406   1288.1729
1295.1011   1309.1538   1324.2657
1344.2580   1345.5751   1354.1215
1358.8258   1359.3191   1372.2638
1379.0558   1385.1737   1388.4872
1396.2557   1410.0033   1418.3170
1422.0938   1452.0765   1458.6003
1486.5408   1492.7601   1506.3209
1509.2589   1510.9918   1518.9583
1520.4697   1534.1425   1542.3592
1549.8698   1573.2209   1589.2442
1614.5836   1620.2250   1628.3076
1631.0057   1644.6293   1652.4765

1658.8164	1663.2864	3011.5033
3018.2209	3051.7926	3064.7841
3082.1795	3091.7842	3107.1153
3128.7807	3184.7310	3191.4496
3194.0503	3198.0372	3199.4574
3201.8098	3209.2195	3213.8185
3218.6730	3220.3584	3221.3089
3231.4092	3241.9265	3270.1833

A2-M1

45.8128	50.8825	71.4846
89.4913	117.8125	122.4546
139.8529	161.8152	184.2507
194.9807	208.1551	216.1223
230.4302	259.5067	281.7092
287.1397	301.7462	311.2796
334.6072	348.5150	359.4708
375.8337	381.0979	387.6753
400.1193	409.9692	430.4270
443.8845	462.4525	488.2861
494.6322	508.4767	510.0968
522.4497	527.8372	533.7363
552.6834	560.8647	571.4320
592.4540	603.3364	612.1216
627.8503	631.6009	643.5612
653.6170	673.3971	683.2092
702.0662	708.6410	712.7854
723.1807	727.1889	734.6572
746.6948	762.0634	771.4518
780.5809	788.7987	793.0552
809.1982	814.8954	827.4354
835.2466	845.4973	846.9898
864.1832	871.3096	886.0177
894.1739	899.4977	900.3989
928.8887	942.0124	948.7841
957.6437	963.9227	983.2732
985.9413	999.4151	1001.6922
1033.6480	1051.9046	1056.5679
1061.4985	1066.3975	1079.2303
1093.4599	1111.1325	1130.6021
1140.1598	1152.9368	1179.2563
1189.9198	1197.9589	1200.1197
1202.4271	1208.3355	1215.6988
1222.2367	1237.2139	1245.7903
1252.3422	1272.8132	1289.6106
1291.5123	1300.7045	1304.1155
1320.4426	1343.3776	1350.7481
1357.6569	1364.7878	1368.2519
1375.9005	1378.9591	1390.4505
1399.4709	1403.9126	1407.1259
1412.9917	1430.7470	1438.4134

1444.5072	1450.7129	1460.8277
1476.3798	1489.5046	1490.5045
1503.5184	1505.6042	1511.2797
1512.8629	1516.3523	1531.7540
1539.1246	1553.3108	1562.1884
1582.8122	1603.6678	1615.7954
1631.4524	1636.3646	1642.3023
1657.7656	1662.1102	1664.9763
2994.6568	3001.7734	3007.0033
3013.0978	3076.2545	3076.5393
3080.9061	3099.6245	3166.9455
3167.1528	3176.4838	3181.0062
3184.4226	3196.7601	3198.1411
3219.5193	3225.8648	3239.6334
3257.3018	3277.1380	3657.0321

A2-M2

28.7958	42.6222	65.3011
86.8654	107.2854	113.9469
117.0658	156.9711	177.8113
193.9819	202.1690	215.8522
224.7146	266.0803	279.0209
294.8784	307.7091	323.1265
346.2831	352.1510	363.9732
371.2240	377.0228	382.2370
401.1225	414.0118	446.3983
450.1457	458.9551	471.9944
486.7211	495.0288	497.9317
514.8799	532.3763	543.5606
553.7594	568.1822	572.3312
578.8576	593.5994	606.1522
613.6546	627.7743	632.5566
637.6368	664.0456	682.1626
691.7353	701.4236	716.1203
724.2422	736.5015	741.8759
749.2943	753.8687	765.7097
770.8489	785.8128	789.6462
805.9318	811.7731	819.1542
820.7286	837.7448	844.5256
851.5056	854.2948	878.1878
883.9281	893.7211	910.5849
931.8717	934.4231	937.4461
941.1653	948.6430	963.1345
971.7640	989.0883	1010.8341
1028.0106	1044.0123	1050.3274
1063.4453	1071.7620	1082.9265
1085.2011	1141.1047	1148.9233
1162.5984	1183.2858	1186.4112
1192.9864	1200.8362	1205.6927
1208.7588	1221.1218	1225.2506
1234.6391	1242.0025	1246.8070

1262.0687	1277.2290	1279.4508
1288.9512	1297.0396	1307.9125
1323.7216	1344.1157	1347.7504
1354.9102	1356.2885	1362.0577
1371.7901	1384.6045	1387.3425
1396.0022	1403.4631	1409.2039
1412.3981	1423.1168	1434.0723
1436.1810	1450.3821	1470.6045
1487.1787	1501.5670	1503.7935
1506.5221	1512.0634	1513.4929
1516.2679	1519.4743	1532.8139
1541.6612	1567.7233	1590.5067
1613.7493	1623.8872	1624.2065
1638.6945	1645.5729	1647.2981
1658.4461	1666.5743	1666.9523
2998.2203	3001.4466	3009.9978
3012.5465	3075.8126	3077.8381
3079.1779	3079.8121	3165.2667
3168.3420	3173.2626	3179.8803
3180.8587	3185.4064	3190.4197
3204.6117	3206.6794	3221.8645
3225.3693	3248.5669	3653.5052

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28.2944	53.4360	72.4822
86.9368	100.4391	109.3499
118.9179	160.5365	182.0758
199.1774	211.2720	223.4456
227.3312	244.8533	279.1120
288.3916	300.2591	322.1227
334.3624	352.5487	361.8635
372.0913	373.7699	386.1660
402.5798	404.1517	445.0449
454.4826	458.7524	474.3813
484.4523	497.0950	500.9828
517.4488	532.5316	542.9768
553.3633	565.7102	574.5537
581.2283	593.6198	602.1950
609.7645	625.9985	637.0134
644.3334	669.8288	676.0659
689.1730	693.6566	715.3029
724.0687	738.8890	748.5000
758.7386	761.7278	776.1213
784.4211	786.8116	801.7092
806.9359	809.6285	823.2007
830.0007	843.4056	849.9915
859.2870	860.2921	868.7416
885.1870	892.9761	924.7342
928.2118	938.0171	940.7285
943.6740	944.3774	961.0149
966.8677	986.3307	999.3843

1017.6320	1043.1580	1046.3467
1062.1155	1064.5871	1076.4110
1104.2293	1136.2134	1149.7776
1165.8975	1183.2943	1187.8227
1192.5876	1201.7999	1206.3353
1208.3995	1219.3907	1227.8373
1234.5725	1246.9891	1253.6341
1267.7077	1273.5028	1278.4353
1282.1680	1298.9333	1312.5374
1320.1223	1342.6668	1345.0953
1354.7664	1360.1425	1368.8577
1370.6108	1378.9302	1387.2993
1395.9882	1408.0951	1408.6034
1413.6396	1418.3018	1433.3597
1443.9046	1449.4606	1484.4648
1487.8537	1495.2051	1503.6702
1506.8036	1511.9886	1513.2622
1515.9350	1517.2306	1534.9005
1540.9390	1560.2842	1587.5044
1621.2627	1624.8659	1632.4569
1638.7954	1644.3308	1649.0989
1657.6566	1666.1364	1672.4247
2997.8340	3001.6382	3009.8089
3012.7199	3075.5448	3078.7687
3079.2525	3079.3961	3165.7546
3167.9236	3170.5473	3172.5346
3179.9227	3184.9876	3185.7344
3191.2427	3196.0662	3208.0880
3208.9682	3227.4370	3663.1071

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28.5782	59.4079	95.7703
113.5012	128.8334	149.6120
175.2132	208.7496	215.8588
263.0581	265.8151	284.5888
319.3991	325.1699	326.5820
359.3800	361.2169	373.1213
423.3200	452.6204	467.6628
481.5854	486.7206	504.5605
515.8074	536.2894	551.0956
564.1781	577.4378	608.7921
615.5531	644.5922	648.5178
666.9523	677.5946	693.7604
711.8380	763.5091	768.8353
770.4637	794.8491	813.2774
820.2737	838.0941	849.6692
857.2042	863.6455	882.0476
885.9058	890.5489	902.2207
915.9387	938.8769	965.6307
970.4158	971.9120	982.4496
1025.2437	1046.6721	1080.4715

1094.1999	1110.2752	1114.7486
1124.8524	1157.8243	1171.7344
1190.3025	1201.8472	1207.6305
1211.8957	1225.4552	1228.2640
1248.5074	1254.9974	1290.7067
1294.5786	1298.6662	1321.1280
1328.4025	1350.0329	1374.7534
1388.1511	1390.4294	1393.1759
1395.1185	1405.3082	1407.7041
1413.7497	1423.3462	1454.3197
1489.8941	1501.3835	1510.1849
1512.8581	1518.1744	1521.8451
1533.2305	1548.7596	1575.3288
1617.5055	1634.5901	1645.6863
1649.9375	1653.9903	1669.5099
3003.0622	3007.4337	3024.8441
3030.8908	3060.3549	3061.8186
3075.3340	3078.8725	3165.5288
3177.6137	3185.1799	3194.8160
3195.2732	3213.3405	3225.0154
3231.5621	3234.8330	3750.7764

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45.8272	59.4707	76.2974
105.8674	124.0204	150.7670
189.8588	211.5446	229.2222
237.9428	266.7392	295.6915
314.3042	327.4456	335.1013
354.0163	370.1812	378.9213
431.1892	452.2065	456.1435
464.9144	483.2761	499.5613
521.5026	537.5682	562.9223
574.5815	584.5116	602.7733
611.6834	629.3041	648.8527
665.8319	673.3762	709.8762
731.3572	737.4041	763.4288
775.0685	802.5002	811.5928
818.8475	837.5673	848.6321
857.3440	862.3484	884.5205
888.6994	892.7477	917.8200
919.5142	934.9682	944.3770
961.8996	974.6407	984.7108
1011.0377	1036.3213	1090.5984
1094.5776	1106.7518	1113.7708
1129.7496	1162.4821	1172.1725
1191.6636	1200.8016	1209.6833
1217.0407	1233.9332	1246.8599
1262.4216	1280.7811	1291.0827
1296.5625	1299.1844	1309.9547
1338.7966	1349.5621	1361.2359
1367.9636	1379.7861	1387.1062

1390.5501	1399.9769	1412.4408
1431.7045	1440.7586	1454.0489
1479.6406	1503.4988	1510.6855
1512.6584	1522.0829	1531.2504
1533.1310	1541.3319	1565.8164
1617.3367	1626.3776	1637.8200
1645.7394	1672.5192	1677.9022
3004.3254	3007.8334	3024.4666
3030.6683	3063.3382	3064.9804
3075.0332	3078.5791	3169.6006
3175.8461	3179.3067	3194.8102
3198.7437	3212.3296	3222.6205
3230.6910	3238.3375	3754.1841