Supplementary Information

General

The atom labelling in the main text and the Supporting information is different in some cases. It is indicated in the descriptions of Tables, to which numbering scheme it refers.

Computational methods

Quantum-chemical calculations were performed using the Gaussian 03 and Gaussian 09[1] program packages. Molecular force-field calculations complemented almost all these computations (we failed to obtain frequencies only at the B3LYP-D3/cc-pVTZ level). Structural parameters for models I and II are listed in tables S4 and S5, respectively (numbering scheme is given at Fig. S1). A smooth potential function (Fig. 3, paper) was obtained using Integral(Grid=SuperFineGrid) in the calculations.

Quantum-chemical calculations applying Grimme's PBEh-3c functional were carried out using Turbomole (Version 7.0.1) with def2-mSVP basis sets for all elements and including D3 dispersion correction with Becke-Johnson damping and three body dispersion terms, as published. Additionally, SCF convergence was increased to 10^{-10} Hartree and combined with a significantly finer DFT grid (m5) to increase accuracy. Cartesian coordinates of all structures are given in Tables S1, S2 and S3.

Additional calculations with use of the functionals CAM-B3LYP, LC-BLYP and M06 accounting for non-covalent interactions were performed for model I in order to assess the differences between the corresponding structural parameters calculated in different approximations. The results are listed in Table S4. All these methods tend to decrease the values of bond lengths as compared to B3LYP functional.

Table S1. Cartesian coordinates of model I of 1,8-BTMSA from PBEh-3c calculations (atom numbering see Figure S1).

C	0.964729560829835	1.758784213177040	0.005043869596142
C	2.354730619183405	1.758814586075469	0.056180499213217
C	3.054420334813193	3.004860172225075	0.061485772815596
C	2.328319100360349	4.189081947167072	0.011721736817344
C	3.122729868063505	0.544983793279580	0.104872145292225
C	4.491142248881557	0.604396291605874	0.158511818897336
C	5.171069794730028	1.842658023294667	0.165826293724049
C	4.474898964363433	3.009144916284629	0.118136508905989
C	0.240721698804678	2.945544709667162	-0.043653918915416
C	0.939384809811795	4.192059840728264	-0.041790461229575
C	-1.195397625756888	2.968662945421013	-0.095137889531687
C	-1.858072004620177	4.167413114961806	-0.145637632814974
C	-1.155629998165931	5.393104826914636	-0.145887299023540
C	0.202648218793940	5.406777172030466	-0.094968273260954
H	0.434609285978489	0.814066700408003	0.001926945344026
H	2.858906280706704	5.134536432549010	0.014090787181372
H	5.057233562886275	-0.316333451697860	0.195534940169969
H	6.251723080880594	1.851525701818613	0.209251807935682
H	4.993296531111564	3.959934261534154	0.122441542060640
H	-2.938822043383712	4.170618140851472	-0.184961056687175
H	-1.711191915655189	6.320169545764694	-0.186947654376805

H	0.743790694808879	6.344809030552238	-0.093992156966044
C	2.483417591982228	-0.723504794286939	0.097233263602640
C	1.976155864469442	-1.824187651007913	0.091711686212011
Si	1.281548021521560	-3.525978303755318	0.096668645252382
C	-1.941626138242035	1.760256666339044	-0.094111075516165
C	-2.607119044590129	0.747477477253668	-0.094254461346609
Si	-3.662627074060842	-0.756960958524217	-0.107941203669898
C	-0.158864309742851	-3.577709661467920	1.303410714287419
C	0.719761682008000	-3.953540433932870	-1.645840074158401
C	2.639794569962445	-4.703273562474478	0.648767855334422
C	-3.720594194531303	-1.466782457839000	1.631952799993174
C	-5.386707382569788	-0.254507044317292	-0.665036694745993
C	-2.915663936293513	-1.987845957679491	-1.316877602863603
H	-0.936090235487819	-2.863704162086039	1.030398049591488
H	-0.617669094228774	-4.567428026535324	1.330566718238134
H	0.165841326160431	-3.334933146270019	2.315727531298680
H	2.999834858443230	-4.455521491020197	1.647696827817384
H	2.280986213324115	-5.733689076418255	0.673252767026200
H	3.494731794447016	-4.668338937568043	-0.027171155978692
H	1.558264143804712	-3.939592975172243	-2.342933354137192
H	0.276353940015845	-4.950129650984357	-1.682299354821150
H	-0.024235011946317	-3.249051003262337	-2.018346117389031
H	-2.724958552687653	-1.704875599147062	2.006961085458057
H	-4.170198668842941	-0.759509387807624	2.329601585573738
H	-4.312280389753630	-2.383274391943263	1.663394283649197
H	-2.895146221405540	-1.582528489625917	-2.329051419866767
H	-1.889915178376418	-2.239219137860110	-1.046636675717034
H	-3.486110116826154	-2.917617380106004	-1.342640633170199
H	-5.825320456656681	0.479255261870259	0.011834302464131
H	-5.369676917967174	0.186512209853968	-1.662079558711042
H	-6.056500755752262	-1.115555335237434	-0.696163178627591

Table S2. Cartesian coordinates of model II of 1,8-BTMSA from PBEh-3c calculations (atom numbering see Figure S1).

C	0.810666907939529	1.836257672246516	0.004242222387262
C	2.201182685953477	1.836061710755052	0.016369543761829
C	2.899954554927510	3.082895592107295	0.017012573659641
C	2.172212181444268	4.267400153501423	0.012214258724191
C	2.970102614599266	0.622139955337571	0.028611939460565
C	4.339822651261194	0.682951602401441	0.035359110845837
C	5.019235920191466	1.921375415673485	0.032230028031235
C	4.321429960203331	3.087855072898334	0.025888056764584
C	0.085256578541597	3.023308868010094	-0.005526939836484
C	0.782240040168502	4.270248928907870	0.003058234711037
C	-1.352087410679243	3.044928926423565	-0.020512985801111
C	-2.018621866492358	4.242005214295913	-0.023792657702836
C	-1.317506423422918	5.468697272017614	-0.012433801576109
C	0.041803804640556	5.484157782816153	-0.001527876038159
H	0.281257802668685	0.891233469918798	-0.000264643206922
H	2.702553110820987	5.212958066049459	0.014993132016628
H	4.907396501350048	-0.237564137025022	0.044854602832014
H	6.100726725630263	1.930310059194897	0.037958851703233
H	4.839187478917037	4.038971878594476	0.025305500243860
H	-3.100021430810910	4.243559892257473	-0.035717265401134
H	-1.874999525446889	6.395494030771801	-0.015238528131948
H	0.580902249640873	6.423308727586501	0.005090376243221
C	2.340995900995599	-0.652391900537391	0.041768945363230
C	1.868938756284571	-1.768991946542089	0.060611554040326
Si	1.321090473851308	-3.524339824031906	0.117842891620947
C	-2.080084605951802	1.826785698816878	-0.040599586865892
C	-2.692819358092703	0.781915148619111	-0.064559195530444
Si	-3.548264054066432	-0.842358133051207	-0.129580284295082
C	-0.118952465297862	-3.686237539397061	1.315054165427926
C	0.824230567036318	-4.067982639473998	-1.612016780223181
C	2.782223652802391	-4.543230847157104	0.722824808531270

C	-3.579239650232009	-1.565040933502276	1.605702863180424
C	-5.296914879243831	-0.583060764944594	-0.768362341586859
C	-2.563941734804648	-1.931502561083250	-1.305795662459757
H	-0.983039909186784	-3.104920739352985	0.994279288298353
H	-0.439152808628373	-4.726071576768327	1.399607247283923
H	0.156172061438032	-3.344051865132213	2.313205377272090
H	3.102172308635624	-4.227851422094064	1.716321419153225
H	2.526953171593207	-5.602818879517501	0.779028769023966
H	3.638468834677030	-4.445536063744896	0.054836579126917
H	1.659543704129244	-3.977930074371307	-2.307193405770617
H	0.503048199112502	-5.111023375053361	-1.615744582449173
H	0.002885915012080	-3.470628909887085	-2.007950456787818
H	-2.576321728305956	-1.644487775934821	2.025564205848801
H	-4.165769820545553	-0.940306917298200	2.279939568734939
H	-4.020593849445953	-2.562937065888006	1.612145689688581
H	-2.612551437917220	-1.548458341619510	-2.325698148175650
H	-1.511735845997948	-1.957771601511762	-1.021864215160487
H	-2.933077608749362	-2.958040244586571	-1.316784352476083
H	-5.868555926762062	0.073267900454236	-0.111755760272486
H	-5.292886367985988	-0.132713255811092	-1.761360295541297
H	-5.835409192151078	-1.529563219431651	-0.837602890803824

Table S3. Cartesian coordinates of the transition state (TS) between models I and II of 1,8-BTMSA from PBEh-3c calculations ($\nu_{imag} = -15$ cm^{-1}) (atom numbering see Figure S1).

C	0.8798614	1.8035120	0.0046755
C	2.2702716	1.8030883	0.0340882
C	2.9696774	3.0494462	0.0367759
C	2.2427476	4.2341214	0.0119914
C	3.0386670	0.5890083	0.0625693
C	4.4080338	0.6487801	0.0901540
C	5.0880011	1.8869610	0.0916771
C	4.3909282	3.0536509	0.0668854
C	0.1552559	2.9907510	-0.0222423
C	0.8530444	4.2374255	-0.0169269
C	-1.2815656	3.0133039	-0.0530984
C	-1.9466510	4.2112077	-0.0777446
C	-1.2450045	5.4374648	-0.0718370
C	0.1140433	5.4518677	-0.0431714
H	0.3498910	0.8587162	0.0007755
H	2.7733565	5.1795025	0.0145406
H	4.9747635	-0.2720439	0.1119059
H	6.1692651	1.8956178	0.1140928
H	4.9091106	4.0045214	0.0684835
H	-3.0278520	4.2132481	-0.1017553
H	-1.8017495	6.3644849	-0.0917118
H	0.6540732	6.3904716	-0.0390060
C	2.4045865	-0.6826484	0.0666098
C	1.9163669	-1.7921656	0.0746758
Si	1.3031865	-3.5256932	0.1085715
C	-2.0174589	1.7993932	-0.0628633
C	-2.6545506	0.7688577	-0.0761985
Si	-3.6009791	-0.8055114	-0.1189975
C	-0.1378728	-3.6386656	1.3103276
C	0.7769074	-4.0186298	-1.6279460
C	2.7211412	-4.6161174	0.6905456
C	-3.6429776	-1.5223746	1.6184404
C	-5.3431904	-0.4368249	-0.7221486
C	-2.7188607	-1.9610679	-1.3125117
H	-0.9663526	-2.9972063	1.0112549
H	-0.5201590	-4.6589015	1.3692672
H	0.1625636	-3.3401119	2.3151187
H	3.0594763	-4.3302991	1.6868532
H	2.4197583	-5.6641349	0.7326497
H	3.5775260	-4.5463506	0.0192929
H	1.6157617	-3.9620506	-2.3223774

H	0.4008055	-5.0428174	-1.6473416
H	-0.0112511	-3.3728783	-2.0150781
H	-2.6397116	-1.6717135	2.0175609
H	-4.1704927	-0.8581588	2.3033896
H	-4.1521622	-2.4871362	1.6358598
H	-2.7390830	-1.5638354	-2.3278887
H	-1.6723979	-2.0869196	-1.0359504
H	-3.1777979	-2.9503003	-1.3321833
H	-5.8575274	0.2566607	-0.0565740
H	-5.3309364	0.0094504	-1.7169098
H	-5.9425453	-1.3469204	-0.7762858

Table S4. Structural parameters of model I of 1,8-BTMSA from QC calculations[a] (atom numbering see Figure S1).

	B3LYP/cc-pVTZ	CAM-B3LYP/cc-pVTZ	LC-BLYP/cc-pVTZ	M06/cc-pVTZ
ω_1, cm^{-1}	14.2	12.5	11.7	6.9
Bond lengths				
r(C(1)–C(2))	1.395	1.390	1.380	1.389
r(C(2)–C(3))	1.439	1.428	1.414	1.429
r(C(3)–C(4))	1.393	1.387	1.378	1.388
r(C(2)–C(5))	1.444	1.440	1.434	1.436
r(C(5)–C(6))	1.378	1.366	1.351	1.370
r(C(6)–C(7))	1.413	1.413	1.413	1.409
r(C(7)–C(8))	1.363	1.354	1.341	1.358
r(C(3)–C(8))	1.423	1.423	1.420	1.419
r(C(5)–C(23))	1.422	1.426	1.426	1.419
r(C(23)–C(24))	1.213	1.205	1.195	1.211
r(C(24)–Si(25))	1.844	1.842	1.835	1.841
r(Si(25)–C(29))	1.885	1.874	1.858	1.876
r(Si(25)–C(30))	1.885	1.874	1.857	1.873
r(Si(25)–C(31))	1.885	1.874	1.858	1.873
r(C(1)–H(15))	1.081	1.080	1.081	1.085
r(C(4)–H(16))	1.083	1.083	1.083	1.085
r(C(6)–H(17))	1.081	1.080	1.080	1.082
r(C(7)–H(18))	1.082	1.081	1.081	1.082
r(C(8)–H(19))	1.082	1.082	1.082	1.084
r(C(29)–H(35))	1.090	1.089	1.088	1.092
r(C(29)–H(36))	1.092	1.091	1.089	1.092
r(C(29)–H(37))	1.091	1.090	1.088	1.091
r(C(30)–H(41))	1.091	1.090	1.088	1.091
r(C(30)–H(42))	1.092	1.091	1.089	1.092
r(C(30)–H(43))	1.091	1.089	1.088	1.090
r(C(31)–H(38))	1.091	1.090	1.088	1.091
r(C(31)–H(39))	1.092	1.091	1.089	1.092
r(C(31)–H(40))	1.091	1.090	1.088	1.091
Angles				
∡(C(1)–C(2)–C(3))	119.1	119.2	119.3	119.3
∡(C(2)–C(3)–C(4))	119.0	119.1	119.2	119.1
∡(C(3)–C(4)–C(10))	122.0	121.8	121.6	121.8
∡(C(9)–C(1)–C(2))	121.8	121.6	121.4	121.5
∡(C(2)–C(5)–C(6))	119.6	119.8	120.0	119.8
∡(C(5)–C(6)–C(7))	121.5	121.4	121.3	121.4
∡(C(6)–C(7)–C(8))	120.4	120.3	120.3	120.3
∡(C(7)–C(8)–C(3))	120.7	120.7	120.7	120.8
∡(C(8)–C(3)–C(2))	119.6	119.5	119.5	119.4
∡(C(3)–C(2)–C(5))	118.2	118.2	118.2	118.3
∡(C(2)–C(5)–C(23))	121.5	121.2	120.8	120.6
∡(C(5)–C(23)–C(24))	177.0	177.4	177.8	178.5
∡(C(23)–C(24)–Si(25))	176.8	177.1	177.5	176.5
∡(C(24–Si(25)–C(29))	108.9	108.7	108.5	106.5
∡(C(24–Si(25)–C(30))	108.7	108.6	108.6	109.3
∡(C(24–Si(25)–C(31))	108.0	108.0	108.0	108.8
∡(C(2)–C(1)–H(15))	119.1	119.2	119.3	119.2
∡(C(3)–C(4)–H(16))	119.0	119.1	119.2	119.1
∡(C(5)–C(6)–H(17))	118.9	119.0	119.1	118.8
∡(C(6)–C(7)–H(18))	119.2	119.2	119.2	119.3
∡(C(7)–C(8)–H(19))	120.7	120.8	120.9	120.9
∡(Si(25)–C(29)–H(35))	111.2	111.2	111.2	110.0
∡(Si(25)–C(29)–H(36))	110.8	110.8	110.8	111.9
∡(Si(25)–C(29)–H(37))	111.0	110.9	110.8	110.5
∡(Si(25)–C(30)–H(41))	110.9	110.9	110.7	110.4
∡(Si(25)–C(30)–H(42))	110.8	110.8	110.8	110.2
∡(Si(25)–C(30)–H(43))	111.3	111.4	111.5	111.8
∡(Si(25)–C(31)–H(38))	111.1	111.0	111.0	110.9
∡(Si(25)–C(31)–H(39))	110.7	110.8	110.8	110.5
∡(Si(25)–C(31)–H(40))	111.1	111.1	111.0	110.9
τ(C(33)–Si(28)–C(11)–C(12))	12.6	14.1	15.4	26.2

[a] Bond lengths are given in (Å), angles in degrees.

Table S5. Structural parameters of model II of 1,8-BTMSA from QC calculations[a] (atom numbering see Figure S1).

	B3LYP-D2/ cc-pVTZ	B3LYP-D3/ cc-pVTZ
ω_1, cm^{-1}	14.0	–[b]
Bond lengths		
r(C(1)–C(2))	1.394	1.395
r(C(1)–C(9))	1.394	1.394
r(C(1)–H(15))	1.081	1.081
r(C(2)–C(3))	1.439	1.438
r(C(2)–C(5))	1.442	1.443
r(C(3)–C(4))	1.394	1.394
r(C(3)–C(8))	1.423	1.424
r(C(4)–C(10))	1.394	1.394
r(C(4)–H(16))	1.083	1.083
r(C(5)–C(6))	1.379	1.377
r(C(5)–C(23))	1.422	1.419
r(C(6)–C(7))	1.414	1.414
r(C(6)–H(17))	1.081	1.081
r(C(7)–C(8))	1.365	1.364
r(C(7)–H(18))	1.082	1.082
r(C(8)–H(19))	1.082	1.082
r(C(9)–C(10))	1.438	1.439
r(C(9)–C(11))	1.443	1.442
r(C(10)–C(14))	1.423	1.423
r(C(11)–C(12))	1.377	1.378
r(C(11)–C(26))	1.419	1.422
r(C(12)–C(13))	1.415	1.413
r(C(12)–H(20))	1.081	1.081
r(C(13)–C(14))	1.365	1.364
r(C(13)–H(21))	1.082	1.082
r(C(14)–H(22))	1.082	1.082
r(C(23)–C(24))	1.213	1.212
r(C(24)–Si(25))	1.843	1.84
r(Si(25)–C(29))	1.884	1.884
r(Si(25)–C(30))	1.884	1.883
r(Si(25)–C(31))	1.885	1.882
r(C(26)–C(27))	1.212	1.213
r(C(27)–Si(28))	1.839	1.843
r(Si(28)–C(32))	1.885	1.883
r(Si(28)–C(33))	1.883	1.884
r(Si(28)–C(34))	1.886	1.882
r(C(29)–H(35))	1.09	1.09
r(C(29)–H(36))	1.094	1.092
r(C(29)–H(37))	1.092	1.091
r(C(30)–H(41))	1.092	1.091
r(C(30)–H(42))	1.094	1.092
r(C(30)–H(43))	1.091	1.09
r(C(31)–H(38))	1.092	1.091
r(C(31)–H(39))	1.094	1.092
r(C(31)–H(40))	1.092	1.091
r(C(32)–H(44))	1.091	1.09
r(C(32)–H(45))	1.093	1.091
r(C(32)–H(46))	1.094	1.092
r(C(33)–H(50))	1.093	1.091
r(C(33)–H(51))	1.092	1.091
r(C(33)–H(52))	1.094	1.092
r(C(34)–H(47))	1.093	1.091
r(C(34)–H(48))	1.091	1.089
r(C(34)–H(49))	1.093	1.092
Angles		
∡(C(2)–C(1)–C(9))	121.6	121.7
∡(C(2)–C(1)–H(15))	119.2	119.2
∡(C(1)–C(2)–C(3))	119.2	119.2
∡(C(1)–C(2)–C(5))	122.4	122.4
∡(C(9)–C(1)–H(15))	119.2	119.1
∡(C(1)–C(9)–C(10))	119.3	119.1
∡(C(1)–C(9)–C(11))	122.4	122.5
∡(C(3)–C(2)–C(5))	118.4	118.3
∡(C(2)–C(3)–C(4))	119.1	119
∡(C(2)–C(3)–C(8))	119.5	119.4
∡(C(2)–C(5)–C(6))	119.6	119.8
∡(C(2)–C(5)–C(23))	121.3	119.9
∡(C(4)–C(3)–C(8))	121.5	121.7
∡(C(3)–C(4)–C(10))	121.8	121.9
∡(C(3)–C(4)–H(16))	119.1	119
∡(C(3)–C(8)–C(7))	120.7	120.8
∡(C(3)–C(8)–H(19))	118.5	118.6
∡(C(10)–C(4)–C(16))	119.1	119
∡(C(4)–C(10)–C(9))	119	119
∡(C(4)–C(10)–C(14))	121.6	121.5
∡(C(6)–C(5)–C(23))	119.1	120.3
∡(C(5)–C(6)–C(7))	121.4	121.3
∡(C(5)–C(6)–H(17))	118.9	119
∡(C(5)–C(23)–C(24))	177.4	178.5
∡(C(7)–C(6)–H(17))	119.6	119.7
∡(C(6)–C(7)–C(8))	120.5	120.5
∡(C(6)–C(7)–H(18))	119.2	119.2
∡(C(8)–C(7)–H(18))	120.4	120.3
∡(C(7)–C(8)–H(19))	120.8	120.6
∡(C(10)–C(9)–C(11))	118.3	118.4
∡(C(9)–C(10)–C(14))	119.4	119.4
∡(C(9)–C(11)–C(12))	119.8	119.6
∡(C(9)–C(11)–C(26))	119.7	121.5
∡(C(10)–C(14)–C(13))	120.7	120.7
∡(C(10)–C(14)–H(22))	118.5	118.6
∡(C(12)–C(11)–C(26))	120.5	118.9
∡(C(11)–C(12)–C(13))	121.3	121.4
∡(C(11)–C(12)–H(20))	119	118.9
∡(C(11)–C(26)–H(27))	177.6	176.7
∡(C(13)–C(12)–H(20))	119.7	119.6
∡(C(12)–C(13)–C(14))	120.5	120.5
∡(C(12)–C(13)–H(21))	119.2	119.2
∡(C(14)–C(13)–H(21))	120.3	120.4
∡(C(13)–C(14)–H(22))	120.8	120.6
∡(C(23)–C(24)–Si(25))	174.4	176.1
∡(C(24)–Si(25)–C(29))	109.5	106.8
∡(C(24)–Si(25)–C(30))	109.3	108.4
∡(C(24)–Si(25)–C(31))	107.6	109.4
∡(C(29)–Si(25)–C(30))	110.6	111.2
∡(C(29)–Si(25)–C(31))	109.9	110.7
∡(Si(25)–C(29)–H(35))	111.6	110.3
∡(Si(25)–C(29)–H(36))	110.2	111.6
∡(Si(25)–C(29)–H(37))	110.9	110.6
∡(C(30)–Si(25)–C(31))	109.9	110.3
∡(Si(25)–C(30)–H(41))	110.8	110.6
∡(Si(25)–C(30)–H(42))	110.3	110.9
∡(Si(25)–C(30)–H(43))	111.4	111.2
∡(Si(25)–C(31)–H(38))	111	111
∡(Si(25)–C(31)–H(39))	110.5	110.6
∡(Si(25)–C(31)–H(40))	111	111
∡(C(26)–C(27)–Si(28))	175.6	173.5
∡(C(27)–Si(28)–C(32))	108.6	109.2

∡(C(27)–Si(28)–C(33))	109.5	107.3
∡(C(27)–Si(28)–C(34))	106.9	109.6
∡(C(32)–Si(28)–C(33))	110.1	110
∡(C(32)–Si(28)–C(34))	111	110.7
∡(Si(28)–C(32)–H(44))	111.3	111.5
∡(Si(28)–C(32)–H(45))	110.6	110.7
∡(Si(28)–C(32)–H(46))	110.7	110.4
∡(C(33)–Si(28)–C(34))	110.6	110
∡(Si(28)–C(33)–H(50))	111.1	110.9
∡(Si(28)–C(33)–H(51))	111	111
∡(Si(28)–C(33)–H(52))	110.6	110.6
∡(Si(28)–C(34)–H(47))	110.6	110.9
∡(Si(28)–C(34)–H(48))	110.5	111.5
∡(Si(28)–C(34)–H(49))	111.5	110.3
∡(H(35)–C(29)–H(36))	107.9	108.4
∡(H(35)–C(29)–H(37))	108.1	107.6
∡(H(36)–C(29)–H(37))	108	108.2

∡(H(41)–C(30)–H(42))	108	108.1
∡(H(41)–C(30)–H(43))	108.2	107.9
∡(H(42)–C(30)–H(43))	108.1	108.1
∡(H(38)–C(31)–H(39))	108.1	108.1
∡(H(38)–C(31)–H(40))	108	108
∡(H(39)–C(31)–H(40))	108.1	108
∡(H(44)–C(32)–H(45))	108	108
∡(H(44)–C(32)–H(46))	108	108
∡(H(45)–C(32)–H(46))	108.1	108.1
∡(H(50)–C(33)–H(51))	108	108
∡(H(50)–C(33)–H(52))	108	108.1
∡(H(51)–C(33)–H(52))	108.1	108.1
∡(H(47)–C(34)–H(48))	107.7	108.1
∡(H(47)–C(34)–H(49))	108.2	108.1
∡(H(48)–C((34)–H(49))	108.2	107.9

[a] Bond lengths are given in (Å), angles in degrees;

[b] We failed to calculate frequencies at B3LYP-D3/cc-pVTZ level

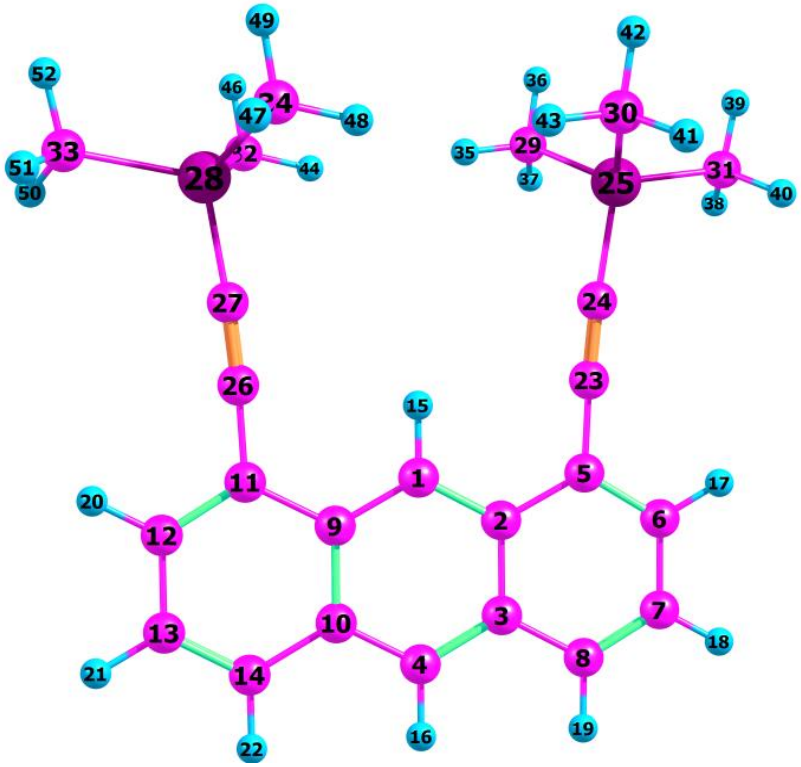
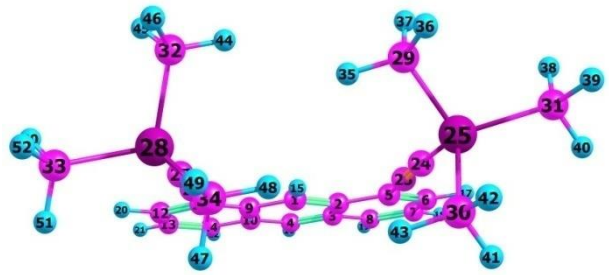
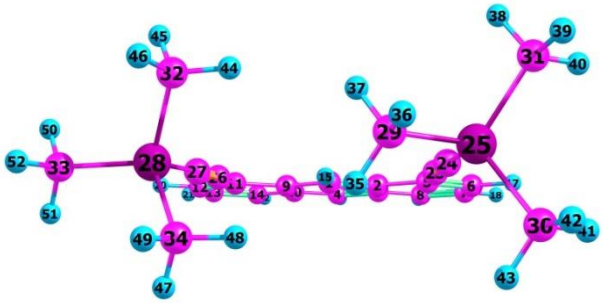


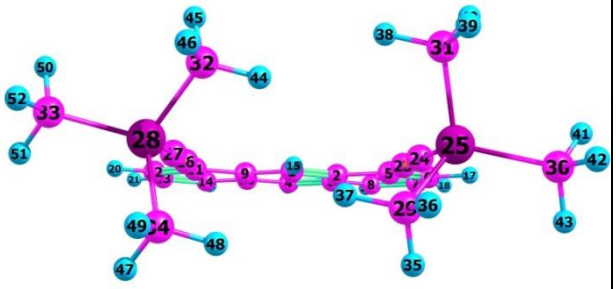
Fig. S1. Atom numbering in 1,8-BTMSA used in Tables S1 to S5.



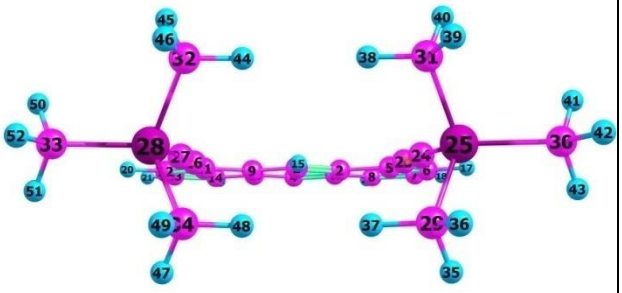
13° (min)



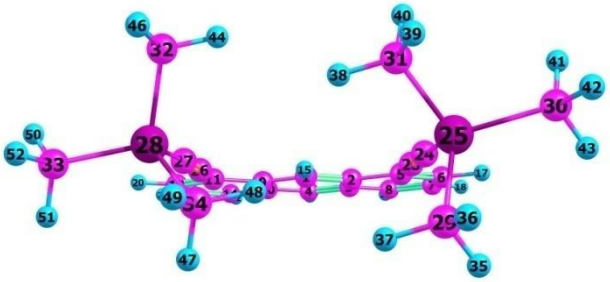
59°(max)



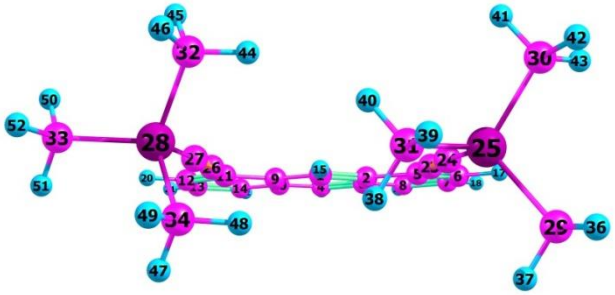
105° (min)



119°(max, local)

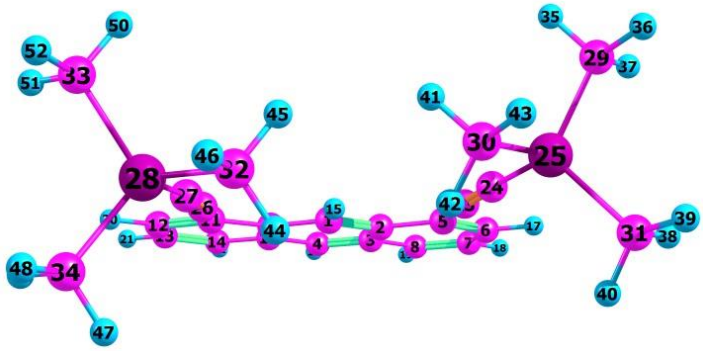


133° (min)



183° (max)

a)



b)

Fig. S2: a) The structures of 1,8-BTMSA corresponding to extrema on PES (Fig. 3 **4**, article);
b) The structure corresponding to the global maximum on PES of 1,8-BTMSA

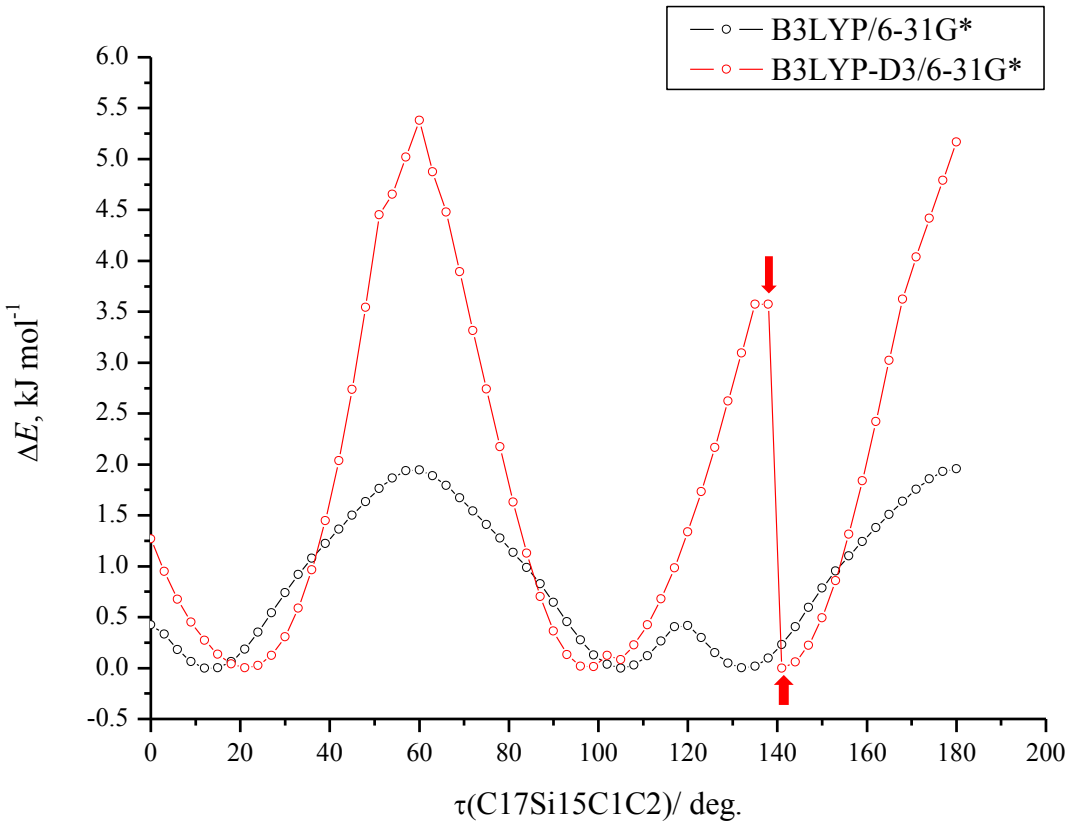


Fig. S3. Comparison of the potential functions calculated with and without accounting for dispersion interactions. The second maximum on the red curve contains a switch to the another side of the PES (two points marked with arrows). Atom numbering here refers to Figure 2 in the main text.

Table S6. Structural parameters of the anthracene fragment for 1,8-BPEA, 1,8-BTMSA and unsubstituted anthracene.[a] Atom numbering here refers to Figure 2 in the main text.

Molecule:	anthracene	1,8-BPEA (model 4)		1,8-BTMSA (model 7)	
Parameter:	B3LYP/cc-pVTZ	B3LYP/cc-pVTZ	GED[8]	B3LYP/cc-pVTZ	GED
r(C(1)–C(2))	1.363	1.379	1.378(6)	1.378	1.374(3)
r(C(1)–C(9a))	1.425	1.444	1.443(6)	1.444	1.448(3)
r(C(2)–C(3))	1.421	1.412	1.411(6)	1.413	1.421(3)
r(C(4a)–C(9a))	1.440	1.438	1.437(6)	1.439	1.436(3)
r(C(4a)–C(10))	1.395	1.394	1.393(6)	1.393	1.396(3)
∢(C(2)–C(1)–C(9a))	121.0	119.5	117.7(30)	119.6	117.3(7)
∢ (C(8a)–C(9)–C(9a))	121.8	121.9	120.4(54)	121.8	119.8(7)
∢ (C(1)–C(2)–C(3))	120.4	121.5	122.8(23)	121.5	120.7(3)
∢ (C(9)–C(9a)–C(4a))	119.1	119.1	120.1 (38)	119.1	120.4(6)

[a] Bond lengths are given in (Å), angles in degrees.

Born-Oppenheimer molecular dynamics (BOMD) calculations

We have performed Born-Oppenheimer molecular dynamics (BOMD) calculations of 1,8-BTMSA at the BLYP-D3/DZVP level of electronic structure theory with empirical dispersion correction.[2] The trajectories were integrated in a microcanonical (NVE) ensemble by the gradient-based velocity-Verlet algorithm[3] with a time step of 0.5 fs for 2500 ps (5000 steps). The electronic structure guess was propagated using the time-reversible scheme.[4] The initial coordinates and velocities have been obtained using quasi-classical normal-mode sampling[5] in the harmonic approximation around the PES minimum. Such approach endows molecules with quantized vibrational energy (including the zero-point correction), allowing it to distribute classically within the system without a contact with a thermal bath (in an NVE ensemble). The vibrational quantum numbers were randomly selected from the Boltzmann distribution at the temperature of the experiment. Overall number of trajectories reported is 20, the final values of distances, amplitudes and vibrational corrections being obtained by both ensemble- and time-averaging.

BOMD calculations have been performed with LSDALTON program,[6,7] whereas for the sampling, Gaussian 09 package has been utilized.[1]

At the same level of theory the simulations in the canonical (NVT) ensemble were performed utilizing the *CP2K* code.[8] The Quickstep method for density functional calculations using a mixed Gaussian and plane waves approach was applied.[9] To model an isolated molecule using this periodic code a single molecule was simulated in a cubic supercell with the size of 17 Å. A chain of five Nose-Hoover thermostats was utilized in the calculations with time constant of 4 fs to regulate the simulation temperature at 408.4 K, approximately the temperature of the GED experiment. The simulations were run with a time step of 0.5 fs and lasted for 25 ps.

Variety of configurations of 1,8-BTMSA observed on the trajectory can be described by large dispersion in the values of the bond angles ∠(Si(15)–C(12)–C(11)), ∠(C(12)–C(11)–C(9a)) and dihedral angles ∠(C(17)–Si(15)–C(1)–C(2)) and ∠(C(22)–Si(16)–C(8)–C(7)) (Fig. S4). Full trajectories are available from ESI.

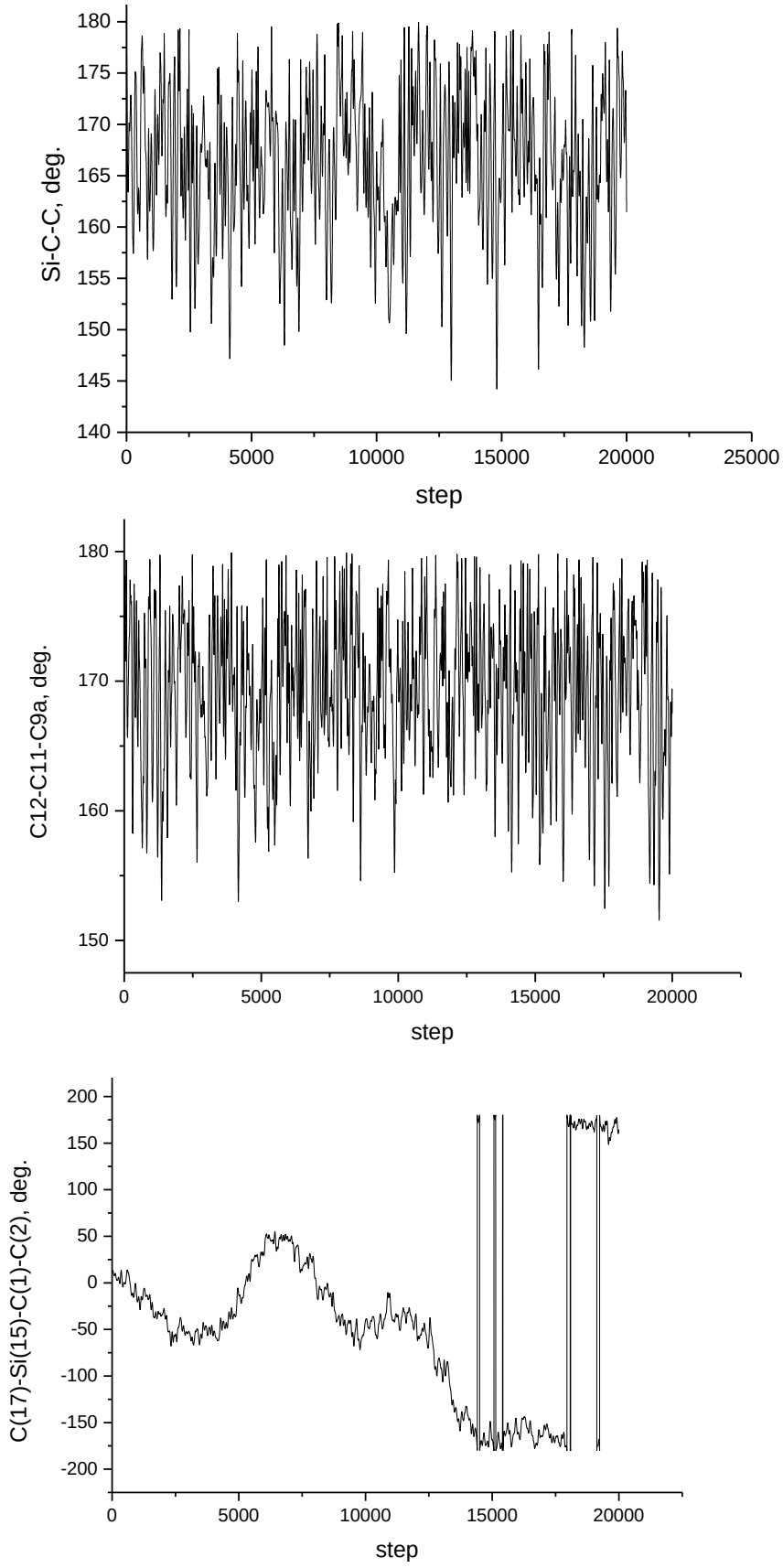


Fig. S4. Variety of the bond angles [$\measuredangle$(Si(15)–C(12)–C(11)) and $\measuredangle$(C(12)–C(11)–C(9a))], and dihedrals [τ(C(17)–Si(15)–C(1)–C(2))] angles for different configurations of 1,8-BTMSA according to the BOMD(NVT) trajectory. Atom numbering here refers to Figure 2 in the main text.

The technique for calculation of vibrational corrections using molecular dynamics data is described in refs.[10,11] The values of selected vibrational corrections and amplitudes calculated using BOMD(NVE), BOMD(NVT) and Shrink are given in the Tables S7 and S8, respectively.

Table S7. Selected bond lengths and vibrational corrections ($\Delta r = r_a - r_e$) for of 1,8-BTMSA.

	r (Å)	Δr (Å)		
	CAM-B3LYP/cc-pVTZ	BOMD(NVE)	BOMD(NVT)	Shrink (rectilinear approximation)
C(1)–H(28)	1.083	−0.018	−0.004	−0.019
C(8)–H(30)	1.082	−0.017	−0.004	−0.022
C(22)–H(38)	1.090	−0.065	−0.026	−0.137
C(23)–H(41)	1.089	−0.006	−0.025	−0.149
C(16)–C(17)	1.205	−0.013	−0.005	−0.022
C(1)–C(4)	1.387	−0.010	−0.005	−0.019
C(11)–C(16)	1.426	−0.015	−0.006	−0.012
Si(18)–C(17)	1.842	0.009	−0.011	−0.055
Si(18)–C(22)	1.874	0.018	−0.014	−0.118

Table S8. Vibrational amplitudes for selected bond lengths of 1,8-BTMSA.

$l_{calc.}$ (Å)	BOMD(NVE)	BOMD(NVT)	Shrink (rectilinear approximation)
C(1)–H(28)	0.065	0.030	0.076
C(8)–H(30)	0.061	0.033	0.076
C(22)–H(38)	0.382	0.422	0.077
C(23)–H(41)	0.386	0.423	0.077
C(16)–C(17)	0.032	0.018	0.036
C(1)–C(4)	0.049	0.032	0.046
C(11)–C(16)	0.049	0.033	0.047
Si(18)–C(17)	0.063	0.046	0.052
Si(18)–C(22)	0.078	0.053	0.056

Conditions of the GED/MS experiment

Table S9. Conditions of the synchronous gas-phase electron diffraction and mass spectrometric experiment.

	1,8-bis[(trimethylsilyl)ethynyl]anthracene	
Nozzle-to-plate distance, mm	338	598
Electron beam current, μA	1.65	0.69
Ionization voltage, V	50	50
Temperature of effusion cell, °C	127(11)	143(12)
Wavelength of electrons, Å	0.03945(4)	0.03991(4)
Exposition time, s	90	40
Residual gas pressure "diffraction chamber/MS-block", Torr	$2.0\cdot10^{-6}$ / $2.4\cdot10^{-7}$	$2.8\cdot10^{-6}$/ $5.5\cdot10^{-7}$
Number of films	5	5
s_{min}–s_{max}; Δs , $Å^{-1}$	2.8–29.8/0.1	1.3–16.8/0.1

Table S10. Mass-spectra of 1,8-BTMSA recorded during two independent GED experiments

Ion	*m*/*e*	Relative abundance, %	
		L_1 = 598 mm	L_2 = 338 mm
$[C_{24}H_{26}Si_2]^+$ ($[M]^+$)	370	37	41
$[M-CH_3]^+$	355	2	2
$[M-2CH_3]^+$	340	2	2
$[M-Si(CH_3)_3]^+$	297	1	1
$[M-2(CH_3)_3]^+$	280	3	3
$[M-Si(CH_3)_3-2CH_3]^+$	267	13	13
$[M-Si(CH_3)_3-3CH_3]^+$	252	2	1
$[C_{17}H_7Si]^+$	239	2	1
$[Si(CH_3)_3]^+$	73	33	31
$[Si(CH_3)_2]^+$	58	1	1
$[Si(CH_3)]^+$	43	3	3

Structural analysis of GED data

The following set of independent parameters was chosen in the refinement (atom numbering here refers to Figure 2 in the main text):

- bond lengths: (C(10)–C(10a)), (C(9a)–C(11)), (C(11)–C(12)), (C(12)–Si(15)), (C(10)–H), (C(17)–H);

- bond angles: ∠(C(4a)–C(10)–C(10a)), ∠(C(8a)–C(10a)–C(10)), ∠(C(12)–C(11)–C(1)), ∠(C(17)–Si(15)–C(12)), ∠(H–C(10)–C(10a)), ∠(H–C(17)–Si(15));

- dihedral angles: τ(C(12)–C(11)–C(1)–C(9a)), τ(Si(15)–C(12)–C(11)–C(1)), τ(C(17)–Si(15)–C(12)–C(2)), τ(H–C(17)–Si(15)–C(12))

The angles: ∠(H–C(10)–C(10a)), ∠(H–C(17)–Si(15)), ∠(C(12)–C(11)–C(1)), τ(C(12)–C(11)–C(1)–C(9a)) and τ(H–C(17)–Si(15)–C(12)) were fixed in the least-squares analysis at the calculated values.

As far as the C–C bond lengths (1.36–1.45 Å) of 1,8-BTMSA fall under the same peak of its radial distribution curve these distances cannot be resolved accurately. To weaken the correlation between structural parameters, the differences between the bond lengths [all Δ(C–C) in the ring system, Δ(Si–C) in the TMSE groups and Δ(C–H) in the ring system and in the TMSE groups] and also between the bond angles [Δ(∠CCC) in the ring system, Δ(∠CSiC) in the TMSE groups, Δ(∠CCH) in the ring system and in the TMSE groups and ((∠Si–C≡C) – (∠C–C≡C))] were taken from the results of the CAM-B3LYP/cc-pVTZ quantum-chemical calculations and were fixed in the analysis by the least-squares method. Starting values for independent parameters were taken from the above mentioned DFT computation. Dependent parameters were determined in terms of the geometrically consistent r_e structure. The amplitudes were refined in groups corresponding to the different peaks on the radial distribution curve. It is important to notice that starting values for some amplitudes were taken as the following typical values: l(C–H) = 0.075 Å; l(C–C) = 0.045 Å, l(C≡C) = 0.035 Å and $l(\mathrm{H\cdots H})_{\mathrm{Met}}$ = 0.125 Å. The necessity of this substitution was motivated by impossibility of determination of the molecular structure with starting amplitudes obtained from BOMD(NVT): the disagreement factor was about 14.5% because of abnormal values of the some calculated amplitudes $l(\mathrm{C–H})_{\mathrm{Met}}$ (see Table S7). Large vibrational amplitudes corresponding to the atom pairs H···H in the methyl groups happened to be very large too ($l(\mathrm{H\cdots H})_{\mathrm{Met}}$ = 0.5÷0.6 Å). At the same time, the amplitudes $l(\mathrm{C–H})_{\mathrm{Ant}}$ and l(C–C) seem to be underestimated.

Since the molecule turned out to be substantially non-restricted in rotating and bending, the angles ∢(C(1)–C(11)–C(12)), ∢(C(11)–C(12)–Si(15)), τ(C(17)–Si(15)–C(12)–C(2)) that describe the positions of the -C–C≡C–Si- chains were determined using scan procedure (see Fig. S5 and 4 (paper)).

Least-square analysis of the molecular intensity function, $sM(s)$ was performed by the modified KCED-35 program, which is similar to the algorithm described in ref.[12] Figs. 6 and 7 (Paper) display the plots of the $sM(s)$ (molecular intensity curve) and $f(r)$ (radial distribution curve) experimental and theoretical (model) functions. Refined geometrical and vibrational parameters for the gas-phase 1,8-BTMSA are listed in Table S11.

Table S11. Structural parameters of 1,8-BTMSA determined by QC calculations and GED experiment (atom numbering here refers to Figure 2 in the main text)

Parameters[a]:	DFT/cc-pVTZ		GED[b] (R_f=4.5%)					
	B3LYP	CAM-B3LYP	r_e, $\angle_e$	r_g	r_a	$r_e - r_a$	l_{exp}	l_{calc}[d]
Bond lengths:								
C(10)–C(10a)[c]	1.393	1.387	1.396(3)	1.402(3)	1.401	–0.00492	0.048(1)	0.032
C(4a)–C(9a)	1.439	1.428	1.436(3)	1.443(3)	1.441	–0.00505	0.048(1)	0.037
C(9)–C(9a)	1.395	1.390	1.398(3)	1.405(3)	1.404	–0.0061	0.048(1)	0.033
C(4)–C(4a)	1.423	1.423	1.431(3)	1.437(3)	1.435	–0.00461	0.048(1)	0.032
C(3)–C(4)	1.363	1.354	1.362(3)	1.368(3)	1.366	–0.00382	0.048(1)	0.028
C(2)–C(3)	1.413	1.413	1.421(3)	1.427(3)	1.425	–0.00359	0.048(1)	0.031
C(1)–C(2)	1.378	1.366	1.374(3)	1.381(3)	1.379	–0.00481	0.048(1)	0.029
C(1)–C(9a)	1.444	1.440	1.448(3)	1.456(3)	1.454	–0.00621	0.048(1)	0.034
C(1)–C(11)[c]	1.422	1.426	1.420(6)	1.428(6)	1.426	–0.00610	0.048(1)	0.033
C(11)–C(12)[c]	1.213	1.205	1.210(5)	1.216(5)	1.215	–0.00461	0.038(1)	0.018
C(12)–Si(15)[c]	1.844	1.842	1.830(4)	1.842(4)	1.841	–0.01059	0.054(1)	0.046
Si(15)–C(17)	1.885	1.874	1.862(4)	1.878(4)	1.876	–0.01364	0.061(1)	0.053
C(10)–H[c]	1.083	1.083	1.083(7)	1.092(8)	1.087	–0.00395	0.078(1)	0.030
C(15)–H[c]	1.092	1.091	1.090(5)	1.141(5)	1.136	–0.04517	0.078(1)	0.460
Angles:								
C(8a)–C(9)–C(9a)	121.8	121.6	119.8(0.7)					
C(9a)–C(1)–C(2)	119.6	119.8	117.3(0.7)					
C(4a)–C(4)–C(3)	120.7	120.7	120.2(0.3)					
C(4a)–C(10)–C(10a)[c]	122.0	121.8	121.3(0.3)					
C(9a)–C(4a)–C(4)	119.6	119.5	119.5(0.4)					
C(9a)–C(1)–C(11)	121.5	121.2	120.7(0.3)					
C(12)–Si(15)–C(17)[c]	108.0	108.0	109.1(1.3)					
(C(1)–C(11)–C(12))	177.0	177.4	178.2(6.0)[e]					
(C(11)–C(12)–Si(15))	176.8	177.1	178.2(6.0)[e]					
τ(C(17)Si(15)C(12)C(2))	13.1	14.5	7.1(40.0)[e]					

[a] Bond lengths and vibrational amplitudes are given in (Å), angles in degrees. See Fig. 4 (Paper) for atom numbering;

[b] Experimental errors are given as $\sigma = [(0.002r)^2+(2.5\sigma_{LS})^2]^{1/2}$ for distances and $\sigma = 3\sigma_{LS}$ for vibrational amplitudes and angles;

[c] Independent parameters;

[d] Vibrational amplitudes calculated from BOMD(NVT).

[e] The angles determined by scan procedures

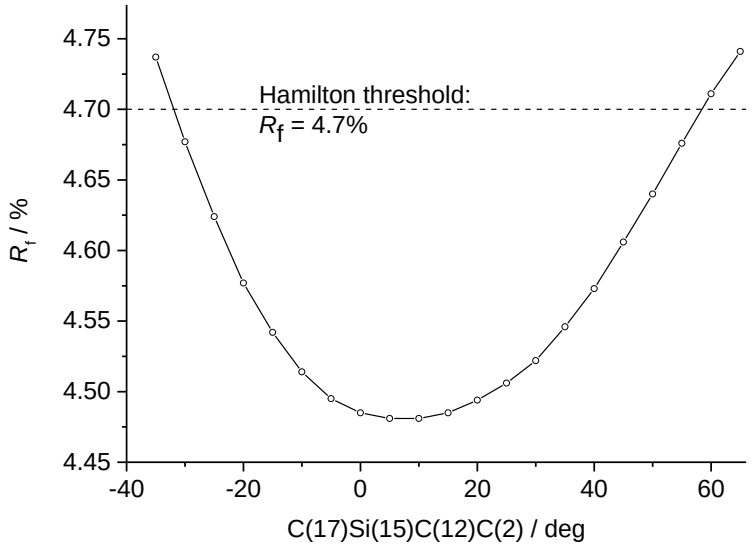


Fig. S5. Shallow minimum of the R_f function in dependence of the torsional angle τ(C(17)–Si(15)–C(12)–C(2)) (atom numbering here refers to Figure 2 in the main text)

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