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Part A. Experimental. Syntheses of compounds V, VI and VII.

Proton and carbon-13 NMR spectra were collected using a Varian 300 MHz NMR. The GC/MS spectra were run on the HP 5890A ion selective detector equipped with a DB-1 column. Infrared spectra were obtained from a Perkin Elmer Spectrum BX spectrometer. Melting points were determined on a Mel-Temp capillary apparatus and are uncorrected. Solvents for reactions were reagent grade, from Fisher. Photo irradiation (cyclization) was accomplished in a Pyrex photolytic cell with a 450-W Ace glass medium pressure mercury vapor lamp.

Trans-1-(*p-tert*-butylphenyl)-2-(2-benzo[c]phenanthrenyl)ethylene (**VII**)

To a stirred solution of 2-benzo[c]phenanthrylmethyltriphenylphosphonium bromide (**2**)[1] (3 g, 5.3 mmol) and *p- tert* -butylbenzaldehyde (**1**, from Aldrich Chemical Co.) (0.9 g, 6.4 mmol) in absolute methanol (60 mL) was added lithium methoxide (0.25 M) in methanol. Almost immediately after the addition a precipitate could be seen in the solution. The mixture was stirred for one hour at room temperature and then water was added (25 mL). The solid was collected by vacuum filtration to yield the crude product. The yellow-brown solid was purified by chromatography on a silica column using *n*-hexane as eluent to give the product (**VII**).

GC/MS (EI, *m*/*z*): M^+ = 386; ^{1}H-NMR ($CDCl_3$, δ): 8.99 (s, 1H), 8.41 (d, 1H, 8.4 Hz), 7.9-7.3 (m, 13H), 6.86 (d, 1H, 12.1 Hz), 6.75 (d, 1H, 12.1 Hz), 1.28 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, δ): 136.0, 135.4, 120.9, 119.8, 119.6, 118.7, 118.5, 118.1, 116.0, 115.5, 114.2, 114.0, 113.8, 113.7, 113.5, 113.0, 112.9, 112.7, 112.3, 111.9, 111.5, 111.4, 111.0, 110.8, 110.6, 108.4, 19.8, 16.5 ppm; FT-IR (nujol, cm^{-1}): 3049, 1909, 1789, 1698, 1603, 961, 842.

1,1′-(2,7-Naphthyl)-2,2′-(3,5-di- *tert* -butylphenyl)ethylene isomers (**6**)

To a stirred solution of 2,7-naphthyldimethyltriphenylphosphonium bromide (**3**)[2] (1 g, 1.2 mmol) in dry THF (7 mL) was added *n*-butyllithium (1.6 M, 3 mL). After stirring for 2 h, 3,5-di- *tert* -butylbenzaldehyde (**4**, from Aldrich Chemical Co.) (0.55 g, 2.5 mmol) in THF (3 mL) was added, and the mixture was stirred for 2 h. A solid precipitate was collected by vacuum filtration and used directly in the next step.

Trans-1-(3,5-di-*tert*-butylphenyl)-2-(3,4-benzo-5,7-di-*tert*-butylphenanthrenyl)ethylene (**VI**)

A solution of **6** (40 mg, 0.01 mmol) in benzene (300 mL) with iodine (0.1 g) and propylene oxide (10 mL) was irradiated for one hour using a 450-Watt mercury vapor lamp and then checked by GC/MS to monitor product formation. Purification by crystallization gave suitable crystals (**VI**) for XRD single crystal analysis.

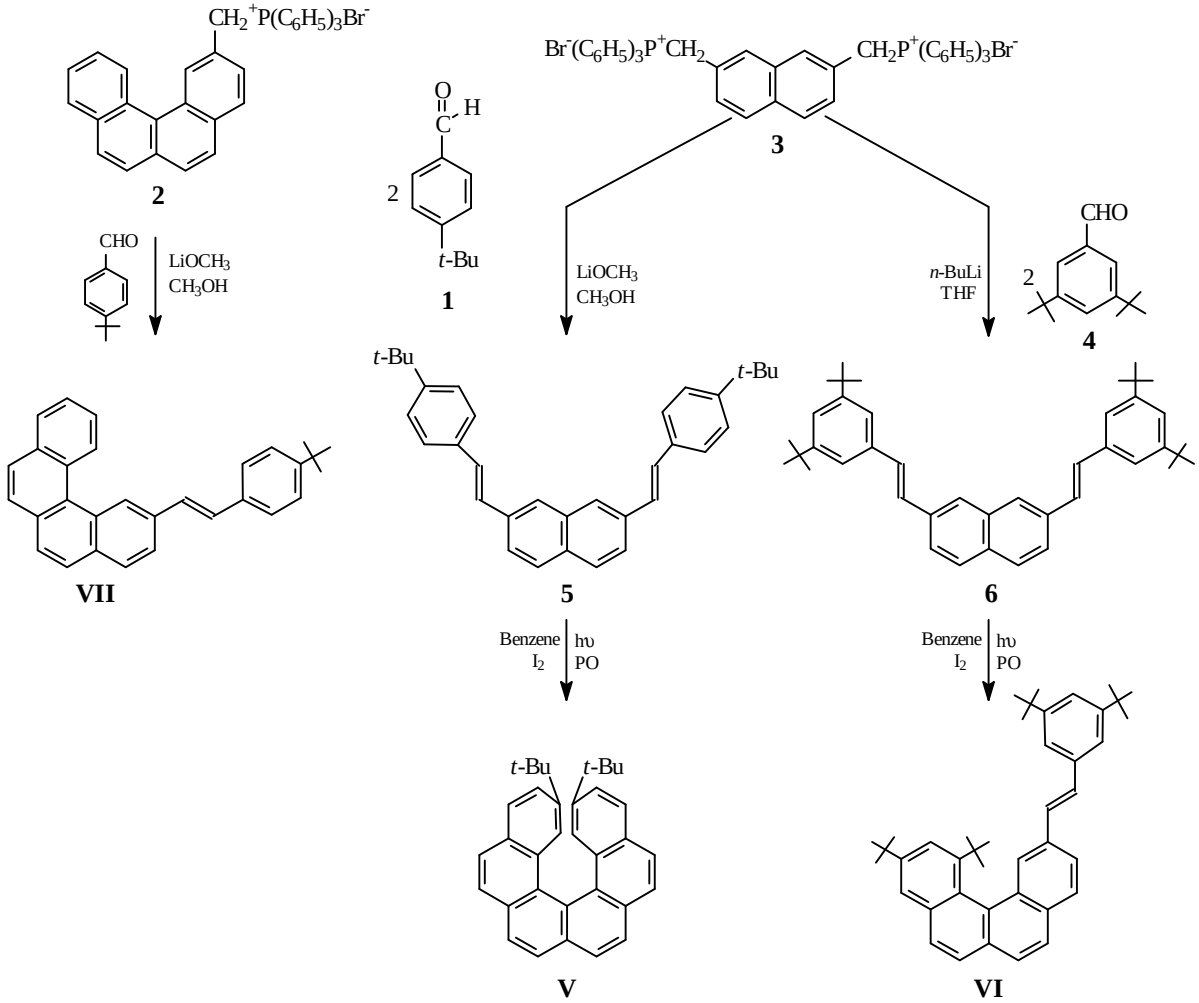
1,1′-(2,7-Naphthyl)-2,2′-(*p-tert*-butylphenyl)ethylene isomers (**5**)

To a solution of 2,7-naphthyldimethyltriphenylphosphonium bromide (**3**)[2] (1 g, 1.2 mmol) and *p- tert* -butylbenzaldehyde **1** (0.4 g, 2.6 mmol) in absolute methanol (20 mL) was added lithium methoxide (1 M, 15 mL) in methanol. Almost immediately after the addition a precipitate could be seen in the reaction mixture. The mixture was stirred for one hour at room temperature; then water was added (5 mL). The solid was collected by vacuum filtration to yield the crude product. The yellow-brown solid was chromatographed on a flash column of silica (*n*-hexane eluent) to give the product (**5**). GC/MS (EI): [M^+] = 444.

(+/–) 2,15-di-*tert*-butylhexahelicene (**V**)

A solution of **5** (40 mg, 0.01 mmol) in benzene (300 mL) with iodine (0.1 g) and propylene oxide (10 mL) was irradiated for one hour using a 450-watt mercury vapor lamp, while checking the disappearance of **5** by GC/MS. The desired product (**V**) was formed and isolated by flash chromatography on a silica column (hexanes eluent) to give **V** (10 mg, 33%).

mp = 276-275.5°C; GC/MS (EI): $[M^+]$ = 440; ^{1}H-NMR ($CDCl_3$) δ: 7.98 (d, 2H, 8.2 Hz), 7.97 (d, 2H, 8.1 Hz), 7.90 (d, 2H, 8.5 Hz), 7.86 (d, 2H, 8.4 Hz), 7.77 (d, 2H, 8.4 Hz), 7.71 (s, 2H), 7.21 (d, 2H, 8.4 Hz), 0.77 (s, 18H) ppm; ^{13}C NMR ($CDCl_3$) δ: 147.9, 133.4, 131.7, 130.4, 129.8, 128.7, 127.6, 127.5, 126.9, 126.0, 124.7, 124.4, 123.5, 34.5, 30.9 ppm; FT-IR (nujol, cm^{-1}): 3154, 3049, 2963, 2904, 2867, 1792, 1559, 1475, 1381, 908, 735, 650; UV/Vis (CH_2Cl_2, 5×10^{-5} M, nm): 349, 327, 315, 302, 255, 237, 208; Anal. Calc. for $C_{34}H_{32}$: C, 92.72; H, 7.27; Found: C, 92.49; H, 7.29.



Scheme 1. Syntheses of 2,15-di-*tert*-butylhexahelicene (**V**), mono-*tert*-butyl semicyclized (**VII**) and the semicyclized tetra-*tert*-butyl analog (**VI**).

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References

1. Lightner, D.A., Hefelfinger, D.T., Powers, T.W., Frank, G.W.& Trueblood, K.N. (1972). *J. Am. Chem. Soc*. **94**, 3492-3497.
2. (a) Borkent, J.H. & Laarhoven, W.H. (1978). *Tetrahedron* **34**, 2565-2567.
   (b) Baker, W., Glockling, F., McOmie, J.F.W. (1951). *J. Chem. Soc.* 1118-1121.

Table 1A. Experimental details for crystal structures with Cu *K*α radiation or Mo *K*α 293-298K

H-atom parameters were constrained.

	IV(b)	V(b)	V(c)	V(d)	VII(b)
Crystal data					
Chemical formula	$C_{36}H_{58}$	$C_{34}H_{31.98}I_{0.02}$	$C_{34}H_{31.98}I_{0.02}$	$C_{34}H_{31.98}I_{0.02}$	$C_{30}H_{26}$
M_r	490.82	443.11	443.11	443.11	386.51
Crystal system, space group	Triclinic, $P\bar{1}$	Orthorhombic, *Pbca*	Orthorhombic, *Pbca*	Orthorhombic, *Pbca*	Monoclinic, $P2_1/c$
Temperature (K)	293	100	298	298	100
a, *b*, *c* (Å)	10.0239 (7), 10.0397 (7), 9.9982 (7)	9.7674 (2), 16.5340 (3), 30.4455 (5)	9.8880 (6), 16.6917 (10), 30.5802 (18)	9.8836 (3), 16.7096 (5), 30.5719 (10)	15.8991 (5), 15.3550 (5), 8.6220 (3)
α, β, γ (°)	77.364 (2), 60.735 (2), 76.060 (3)	90, 90, 90	90, 90, 90	90, 90, 90	90, 92.677 (2), 90
V (Å^3)	845.83 (10)	4916.77 (16)	5047.2 (5)	5049.0 (3)	2102.60 (12)
Z	1	8	8	8	4
Radiation type	Mo *K*α	Cu *K*α	Mo *K*α	Cu *K*α	Cu *K*α
μ (mm^{-1})	0.05	0.70	0.09	0.68	0.52
Crystal size (mm)	0.4 × 0.3 × 0.25	0.60 × 0.20 × 0.20	0.6 × 0.4 × 0.3	0.60 × 0.20 × 0.20	0.60 × 0.10 × 0.10
Data collection					
Diffractometer	Modified Huber	CCD area detector	CCD area detector	CCD area detector	CCD area detector
Absorption correction	–	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{min}, T_{max}	–	0.744, 0.870	0.811, 1.0	0.690, 0.990	0.855, 0.950
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4925, 4925, 2874	47333, 4366, 4061	29923, 6166, 3865	24764, 4162, 3221	22369, 3653, 3122
R_{int}	0.0000	0.026	0.027	0.032	0.030
Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.085, 0.298, 1.08	0.038, 0.095, 1.02	0.050, 0.161, 1.03	0.049, 0.143, 1.05	0.038, 0.103, 1.03
No. of reflections	4925	4366	6166	4162	3653
No. of parameters	171	331	331	331	274

No. of restraints	0	0	0	0	0
w, where $P = (F_o^2 + 2F_c^2)/3$	$1/[\sigma^2(F_o^2) + (0.1386P)^2 + 0.2807P]$	$1/[\sigma^2(F_o^2) + (0.0393P)^2 + 2.3993P]$	$1/[\sigma^2(F_o^2) + (0.0704P)^2 + 1.1583P]$	$1/[\sigma^2(F_o^2) + (0.0711P)^2 + 1.0652P]$	$1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.4277P]$
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.45, -0.28	0.20, -0.19	0.19, -0.17	0.16, -0.18	0.16, -0.20

	VII(c)	VII(d)
Crystal data		
Chemical formula	$C_{30}H_{26}$	$C_{30}H_{26}$
M_r	386.51	386.51
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	293	296
a, b, c (Å)	15.990 (2), 15.712 (2), 8.6656 (11)	15.9882 (3), 15.7045 (3), 8.6555 (2)
α, β, γ (°)	90, 92.544 (2), 90	90, 92.549 (1), 90
V (Å^3)	2175.0 (5)	2171.13 (8)
Z	4	4
Radiation type	Mo $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	0.07	0.50
Crystal size (mm)	0.60 × 0.10 × 0.10	0.60 × 0.20 × 0.20
Data collection		
Diffractometer	CCD area detector diffractometer	CCD area detector diffractometer
Absorption correction	Multi-scan , *SADABS* (Bruker)	Multi-scan , *SADABS* (Bruker)
T_{min}, T_{max}	0.961, 0.993	0.803, 0.907
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19272, 5390, 3017	11417, 3354, 2528
R_{int}	0.039	0.032
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.055, 0.160, 1.01	0.046, 0.137, 1.06
No. of reflections	5390	3354
No. of parameters	274	272
No. of restraints	0	0
w, where $P = (F_o^2 + 2F_c^2)/3$	$1/[\sigma^2(F_o^2) + (0.0694P)^2 + 0.2605P]$	$1/[\sigma^2(F_o^2) + (0.0698P)^2 + 0.2621P]$
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.24, -0.21	0.29, -0.21

Computer programs: Bruker *SMART APEX2*, UCLA Crystallographic Package, Bruker *SMART*, Bruker *SAINT*, *SHELXS97* (Sheldrick, 1990), *SHELXL97* (Sheldrick, 1997), Bruker *SHELXTL*, Bruker *SADABS*.

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Table 3A. Selected distances (Å), angles (°) and planes in structure **III**(a). See Figures 2 and 3 (main text section **3.1**) for atomic numbering.

Long aliphatic bond distances:	
C1-C2, C1B-C2B	1.580(2), 1.581(2)
Long CAr - Ct bond distances:	
C4-C17, C4B-C17B	1.563(2), 1.563(2)
C8-C25, C8B-C25B	1.572(2), 1.564(2)
Long aromatic bond distances:	
C3-C8, C3B-C8B	1.423(2), 1.427(2)
C3-C4, C3B-C4B	1.432(2), 1.427(2)
Large C_{Ar} - C_{Ar} - C_t bond angles:	
C3-C8-C25, C3B-C8B-C25B	129.3(1), 128.8(1)
C3-C4-C17, C3B-C4B-C17B	123.2(1), 123.5(1)
Large aromatic bond angles:	
C4-C5-C6, C4B-C5B-C6B	123.1(1), 122.8(1)
C6-C7-C8, C6B-C7B-C8B	123.8(1), 123.9(1)
Least-squares planes (rms deviation):	
C3 to C8, C3B to C8B	0.0542(9), 0.0683(9)
C9 to C14, C9B to C14B	0.0029(9), 0.0030(9)
Bridging torsion angle	
C9-C1-C2-C3	-62.9°
C9B-C1B-C2B-C3B	-72.1°
Intramolecular C-H...p contacts:	
C14-centroid C3-C8, C14B-centroid C3B-C8B	3.599, 3.689
C19- centroid C9-C14, C19B- centroid C9B-C14B	3.324, 3.432
Intermolecular C-H...p contacts:	
$C16^{ia}$- centroid C9B-C14B	3.557
$C16B^{ii}$- centroid C9-C14	3.423

[a] Symmetry codes: i = x+1, y, z; ii = x-1, y, z

Table 5A. Selected distances (Å), angles (°) and planes in structure **V**(a). See Figure 5 (main text section **3.3**) for atomic numbering.

Short aromatic "outer" -HC-CH- bond distances:	Average
C3-C4, C5-C6, C7-C8, C9-C10, C11-C12, C13-C14)	1.355(7)
Long aromatic "inner" -C-C- bond distances:	Average
C17-C19, C19-C21, C21-C23, C23-C25	1.456(2)
Large "inner" aromatic bond angles	
C17-C19-C21, C23-C21-C19, C21-C23-C25	124.6(1), 126.0(1), 124.7(1)
Least-squares planes (rms deviation):	
C1-C4, C25-C26; distance of C27 from plane	0.0258; 0.1272
C13-C18; distance of C31from plane	0.0229; -0.0684

Part B. Results: Thermal Motion Analysis

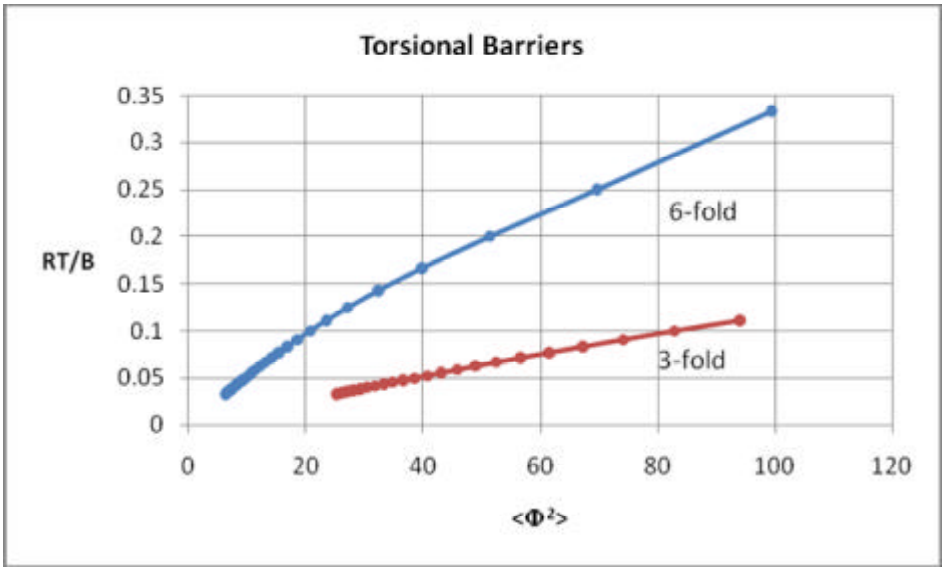

Figure 4B. Torsional barriers (Maverick *et al*, 1991) for the range $\langle f^2 \rangle$ = 0-100 $(°)^2$.

Part B. Results: Search of CSD: Table 7B. Summary of TBG ARG analyses of CSD entries

Refcode	*R-factor*	*Z'*	*r.m.s. su(U)*	*ARG rigidity*	*ARG Type*	*<F ²>*	*Formula*	*Compound Name (L)*
BALXOB01	2.6	0.5	0.0010	0.9, 1.7, 1.1	C, A, B	10.7, 17.1, 8.2	C36 | H58 | P2	1,2-bis(2,4,6-Tri-t-butylphenyl)diphosphene
CIVMOJ10	4	1	0.001(n.g.)	1.8	C	18.1	C36 | H18	9-t-Butylanthracene
CIVZUD	4.63	1	0.0005	1.6,3.0	B,C	7.1, 68.5	C20 | H27 | N | O	2,4-Di-t-butyl-6-(2-pyridylmethyl)phenol
COBROB	3.83	1	0.0007	2	B	4	C23 | H32 | O3 | S	(Ss)-2-(2'-t-Butylphenoxy)-1-methoxymethyl-4-methyl-3-t-butylsulfinylbenzene
COBRUH	3.28	1	0.0007	0.6	B	5.7	C26 | H36 | O3 | S	(Ss)-2-(2'-t-Butylphenoxy)-1-methoxymethyl-4-methyl-3-(1-methylcyclohexylsulfinyl)benzene
COBSAO	3.12	1	0.0007	2.7	B	6.8	C26 | H36 | O4 | S	P-(-)-2-(2'-t-butylphenoxy)-1-methoxymethyl-4-methyl-3-(1-methylcyclohexylsulfonyl)benzene
DACPON	5.67	0.5	0.0009	4.2, 1.7	C, A	14.6, 18.2	C44 | H52 | O6, 0.68(H2 | O)	5,11,17,23-Tetra-t-butyl-25,26,27,28-tetrahydroxy-2,14-dioxocalix(4)arene hydrate
DIDMAF	4.66	0.5	0.0004	1.3	A	0	C26 | H30	4,4''-Di-t-butyl-o-terphenyl
DIDMEJ	5.46	1	0.0007	2.4, 1.1	A, A	7.6, 1.3	C26 | H28	2,11-Di-t-butyltriphenylene
ERUFAY	4.23	1	0.0010	2.1, 2.2, 1.7	A, A, A	21.8, 26.4, 25.2	C69 | H99 | N3 | O3	1,4,7-tris(3-(Adamantyl)-5-t-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane
ESALUF	5.47	3	0.0009-0.0010	3.7, 1.8, 0.8	B, B, B	9.8, 5.5, 3.2	C11 | H16 | O2	3-t-Butyl-4-hydroxyanisole
ESALUF01	4.35	1	0.0005	3.1	B	0.1	C11 | H16 | O2	3-t-Butyl-4-hydroxyanisole
EXUKEN	4.35	1	0.0010	1.3, 1.7, 1.8, 2.5	A, A-C, A, A	20.1, 66.6, 20.6, 23.8	C48 | H60 | O8, 3(C3 | H7 | N | O)	(5,11,17,23-Tetra-t-butyl-26,28-dihydroxycalix(4)arene-25,27-dioxy)diacetic acid N,N-dimethylformamide solvate
HIGZED	4.72	1	0.0010	1.7	C?	5.2	C16 | H18	6-(p-t-Butylphenyl)fulvene
HOFNIA	4.17	1	0.0007,0.0007	2.0, 1.7	B, B	19.5, 12.8	C21 | H27 | N | O3 | S	2-(3,5-Di-t-butyl-4-hydroxybenzylsulfanyl)nicotinic acid
INIBUC	4.1	1	0.0006-0.0007	1.9, 0.9, 1.4, 1.9	B, B, B, B	7.7, 5.0, 6.0, 2.8	C55 | H64 | O5 | P2	4,5-bis(bis(2-t-Butylphenoxy)phosphino)-9,9-dimethylxanthene
INOCET	4.5	0.5	0.0008	2.1	C	27.8	C23 | H28 | O4	5,5'-Di-t-butyl-2,2'-dihydroxy-3,3'-methylenedibenzaldehyde
JAXHEW	4.24	1	0.0006	0.4, 1.5	A, A	neg., 5.5	C32 | H34	2,2'-bis(4-t-butylphenyl)-1,1'-biphenyl
JAXHIA	6.36	0.5	0.0005-0.0006	1.5, 1.6	A, A-C	neg., neg.	C52 | H58	2,5,2',5'-tetrakis(4-t-butylphenyl)-1,1'-biphenyl
JEHNUG	5.58	1	0.0009	1.7, 0.9, 2.9, 2.1	B, A, B, A	20.3, 9.1, 8.6, 20.6	C36 | H50 | O2, C4 | H10 | O	1,1-bis(3,5-Di-t-butyl-2-hydroxyphenyl)-2-phenylethane 2-methylpropan-2-ol solvate
JEKPAR	6.21	0.5	0.0008	1.8, 1.2	B, A	9.9, 4.9	C32 | H52 | N2 | O2	1,2-bis(2-hydroxy-3,5-bis(t-butyl)benzylamino)ethane
JISXUF	3.55	1	0.0008	1.2	B	0	C22 | H22 | O2	(12bR,M)-12-t-Butyl-5,7,8,12b-tetrahydrobenzo(c)phenanthrene-1,4-dione
JOQJOO	3.83	1	0.0008	3.0, 1.2, 0.8	C, A, C	5.7, 23.5, 7.6	C32 | H49 | O | P	2,4-Di-t-butyl-6-((2,4,6-tri-t-butylphenyl)phosphinidene)-cyclohexa-1,4-dien-3-one

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Table 7B. Summary of TBG ARG analyses of CSD entries, continued

<table>
<tr><th>Refcode</th><th>R-factor</th><th>Z'</th><th>r.m.s. su(U)</th><th>ARG rigidity</th><th>ARG Type</th><th><F ^{2}></th><th>Formula</th><th>Compound Name (L)</th></tr>
<tr><td>KALQAQ</td><td>4.1</td><td>1</td><td>0.0009</td><td>1.7, 1.7</td><td>B, A</td><td>18.9, 7.9</td><td>C24|H31|N|O</td><td>(S,S)-1-(2,5-Di-t-butylphenyl)-3-methyl-3,4-dihydro-1H-quinolin-2-one</td></tr>
<tr><td>KALQEU</td><td>3.88</td><td>1</td><td>0.0008</td><td>1.8</td><td>B</td><td>2.1</td><td>C21|H26|N2|O5</td><td>(S,S)-N-(2-t-Butylphenyl)-2-(methoxymethoxy)-N-(4-nitrophenyl)propanamide</td></tr>
<tr><td>KATKEW</td><td>3.02</td><td>1</td><td>0.0006</td><td>1.8, 0.8</td><td>A-C, A</td><td>5.1, 33.1</td><td>C24|H26|N2|O4|S</td><td>2,5-bis(4-t-butylphenyl)-3,4-dinitrothiophene</td></tr>
<tr><td>LIHTOM</td><td>3.13</td><td>2</td><td>0.0009</td><td>0.3,1.4,1.4, 2.2</td><td>C, C, C, C</td><td>15.1, 15.6, 14.1, 14.2</td><td>C32|H34</td><td>4,4'''-Di-t-butyl-p-quaterphenyl</td></tr>
<tr><td>MIPKOM</td><td>3.96</td><td>1</td><td>0.001</td><td>0.9, 1.7</td><td>A, A</td><td>16.8, 17.5</td><td>C70|H66|Cl2|N4|O6, C|H4|O, 3(C|H|Cl3)</td><td>5,17-bis(2-(4-Chlorophenyl)-4-oxo-3,4-dihydroquinazolin-3-yl)-11,23-di-t-butyl-26,28-dihydroxy-25,27-dipropoxycalix(4)arene methanol clathrate chloroform solvate</td></tr>
<tr><td>MIRGIE</td><td>3.7</td><td>1</td><td>0.0007</td><td>1.1, 1.9, 0.7, 0.6</td><td>B, B, B, B</td><td>3.6, 15.7, 7.3, 25.9</td><td>C32|H50|Mg|O6</td><td>(1,2-Dimethoxyethane)-bis(3,6-di-t-butyl-o-benzosemiquinone)-di-magnesium(ii)</td></tr>
<tr><td>NANLOE</td><td>3.5</td><td>1</td><td>0.0006</td><td>0.7, 2.1</td><td>B, B</td><td>neg., 3.4</td><td>C32|H50|O4</td><td>3,6-di-t-butyl-4-(3,6-di-t-butyl-2-ethoxyphenoxy)-2-ethoxycyclohexa-2,5-dienone</td></tr>
<tr><td>PERPUY</td><td>4.28</td><td>1</td><td>0.0007</td><td>0.1, 2.1, 2.0, 1.7</td><td>A, A, A, C</td><td>15.0, 14.7, 15.9, 20.7</td><td>C50|H64|O8, C3|H6|O</td><td>2,3,16,17-tetrahomo-3,17-dioxacalix[4]arene acetone solvate</td></tr>
<tr><td>QIBDAH</td><td>6.08</td><td>0.5</td><td>0.0010</td><td>0.8</td><td>C</td><td>26.2</td><td>C60|H62|N6|O8, 2(C2|H3|N)</td><td>12,14,16,28,30,32-hexaazaundecacyclo[25.5.2.2$11,17!.1$1,26!.1$7,10!.1$10,17!.1$23,26!.0$3,8!.0$12,16!.0$19,24!.0$28,32!]tetraconta-3,5,7,19,21,23,33,37-octaene-13,15,29,31,36,39-</td></tr>
<tr><td>QIXVIC</td><td>4.7</td><td>0.5</td><td>0.0007</td><td>1.1, 1.0</td><td>A, C</td><td>10.1, 10.6</td><td>C48|H64|O8</td><td>4,5',4",5'''-Tetra-t-butyltetrabenzo-24-crown-8</td></tr>
<tr><td>RALFAM</td><td>5.18</td><td>1</td><td>0.0007</td><td>1.4, 0.8</td><td>B, B</td><td>8.7, 6.6</td><td>C23|H32|O2, C4|H10|O</td><td>2-(3-t-Butyl-2-hydroxy-5-methylbenzyl)-6-t-butyl-4-methylphenol diethyl ether solvate</td></tr>
<tr><td>REPNUV</td><td>3.9</td><td>0.5</td><td>0.0007</td><td>1.4</td><td>A</td><td>24.6</td><td>C38|H44|O2</td><td>5,17-Di-t-butyl-25,27-dimethoxycalix(4)arene</td></tr>
<tr><td>RERWIV</td><td>4.17</td><td>2</td><td>0.0006</td><td>2.4, 2.4</td><td>B, C</td><td>39.5, 14.1</td><td>C19|H22|N2|O3</td><td>N-(2-t-butylphenyl)-N-(4-nitrophenyl)propanamide</td></tr>
<tr><td>SENYAM</td><td>5.68</td><td>1</td><td>0.0004</td><td>5.7, 2.2, 1.9, 0.7</td><td>C, A, B, B</td><td>36.8, 23.9, 12.2, 9.1</td><td>C52|H74|N2|O2</td><td>7a,14a,15a,15b-tetrahydro-14,16-dioxa-5,9-diaza-8,15-ethenohexaphene</td></tr>
<tr><td>SEQBEW</td><td>4.67</td><td>1</td><td>0.0009,0.0011</td><td>0.4, 1.1</td><td>A,A</td><td>0.5, 8.3</td><td>C38|H56|Li2|N2|O4</td><td>bis(mu!2$-5-t-Butyl-2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenylene)-bis(tetrahydrofuran)-di-lithium</td></tr>
<tr><td>VAWDIH</td><td>3.52</td><td>1</td><td>0.0008</td><td>2.1</td><td>A-C</td><td>29.9</td><td>C19|H19|B|F2|N2</td><td>N,N'-Difluoroboryl-5-(4-t-butylphenyl)dipyrrin</td></tr>
<tr><td>VERMIP</td><td>5.18</td><td>1</td><td>0.0007, 0.0006</td><td>4.3, 5.0, 1.4, 2.5</td><td>C, C, A, A</td><td>32.2, 92.4, 30.4, 16.2</td><td>C60|H82|O11, 2(C2|H3|N)</td><td>5,11,17,23-tetra-t-butyl-25,27-bis(ethoxycarbonylmethoxy)-26,28-(3,6,9-trioxaundecane-1,11-diolato)calix[4]arene acetonitrile solvate</td></tr>
<tr><td>WEDVUX</td><td>3.99</td><td>0.5</td><td>0.0004</td><td>0.5, 1.0</td><td>B, B</td><td>5.5, 7.0</td><td>C40|H56|Li2|N2|O4, 2(C5|H5|N)</td><td>bis(mu!2$-2,6-Di-t-butyl-4-methoxyphenoxo)-bis(pyridine-N)-di-lithium pyridine solvate</td></tr>
</table>

Table 7B. Summary of TBG ARG analyses of CSD entries, continued

Refcode	*R-factor*	*Z'*	*r.m.s. su(U)*	*ARG rigidity*	*ARG Type*	*<F ²>*	*Formula*	*Compound Name (L)*
WEDWAE	3.96	1	0.0004	1.4	A	10.6	C22|H18|N2|O	2-(4-t-Butylphenyl)-5-(4-butadiynylphenyl)-1,3,4-oxadiazole
WEWDUY	4.96	1	0.0009	1.2	B	6.2	C22|H30|O3|S	t-Butyl 2-(2-t-butylphenoxy)-3-(methoxymethyl)phenyl sulfoxide
WEXCEI	3.12	1	0.0010	10.8, 1.8	C, B	128.0, 13.6	C29|H31|N|O2	10,12-Di-t-butyl-8b-methoxy-dibenzo(a,c)phenoxazine
XESRUJ	5.58	1	0.001	1.4	C	13.1	C23|H24|N4	4-t-Butyl-2,6-bis(phenyldiazenyl)toluene
XIPJEM	3.39	1	0.0007	1.4, 3.0	A-C,A	8.6, 36.2	C46|H40	2,7-di-t-butylhexabenzo(4.4.4)propellane
ZOJRAR01	3.92	0.5	0.0007	0.4	B	16.1	C12|H16|O2	3-t-butyl-2-hydroxy-5-methylbenzaldehyde

Frey, Khan, Knobler, Lightner, Maverick, Phillips, Rappoport, and Trueblood, Thermal motion of *tert*-butyl groups III: Supplementary Material

Table 7C Rigidity and $<\Phi^2>$ for CSD entries, by TBG type: Types **A**, **B** and **C**

Parameter Values	* = CHNO	** = CH		*** = *p-tert*-butyl phenyl			**** = rejected				
Refcode	ARG rigidity	***ARG Type***	**<F ²>**	ARG rigidity	***ARG Type***	**<F ²>**	ARG rigidity	***ARG Type***	**<F ²>**		other **<F ²>**
BALXOB01							0.9	C	10.7		
	1.7	A	17.1								
				1.1	B	8.2					
CIVMOJ10**							1.8	C	18.1		
CIVZUD*				1.6	B	7.1	3.0	C	68.5****		
COBROB				2	B	4.0					
COBRUH				0.6	B	5.7					
COBSAO				2.7	B	6.8					
DACPON*							4.2	C	14.6****		
	1.7	A	18.2								
DIDMAF**,***	1.3	A	0.0								
DIDMEJ**	2.4	A	7.6								
	1.1	A	1.3								
ERUFAY*	2.1	A	21.8								
	2.2	A	26.4								
	1.7	A	25.2								
ESALUF*				3.7	B	9.8****					
				1.8	B	5.5					
				0.8	B	3.2					
ESALUF01*				3.1	B	0.1****					
EXUKEN*	1.3	A	20.1								
							1.7	A-C	66.6****		
	1.8	A	20.6								
	2.5	A	23.8								
HIGZED**,***							1.7	C	5.2		
HOFNIA				2	B	19.5					
				1.7	B	12.8					
INIBUC				1.9	B	7.7					
				0.9	B	5.0					
				1.4	B	6.0					
				1.9	B	2.8					
INOCET*							2.1	C	27.8		
JAXHEW**,***	0.4	A	26.8							10-atom	neg
	1.5	A	11.8							10-atom	5.5
JAXHIA**,***	1.5	A	26.6							10-atom	neg
							1.6	A-C	18.9	10-atom	neg
JEHNUG*				1.7	B	26.3				14-atom	20.3
	0.9	A	15.2							14-atom	9.1
				2.9	B	10.1				14-atom	8.6
	2.1	A	25.9							14-atom	20.5
JEKPAR*				1.8	B	22.0				14-atom	9.9
	1.2	A	24.9							14-atom	4.9
JISXUF*				1.2	B	0.0				10-atom	0.8
JOQJOO							3.0	C	11.5	18-atom	5.7
	1.2	A	36.9							18-atom	23.5
							0.8	C	11.4	18-atom	7.6

Table 7C Rigidity and $<\Phi^2>$ for CSD entries, by TBG type: Types **A**, **B** and **C**

KALQAQ*				1.7	B	33.0				18-atom	18.9
	1.7	A	22.1							18-atom	7.9
KALQEU*				1.8	B	10.2				10-atom	2.1
KATKEW,***							1.8	A-C	5.1	10-atom	neg
	0.8	A	33.1							10-atom	15.7
LIHTOM**,***							0.3	A-C	15.1	10-atom	neg
							1.4	C	15.6	10-atom	neg
							1.4	C	14.1	10-atom	neg
							2.2	A-C	14.2	10-atom	neg
MIPKOM	0.9	A	16.8							10-atom	9.0
	1.7	A	17.5							10-atom	10.8
MIRGIE				1.1	B	3.6					
				1.9	B	15.7					
				0.7	B	7.3					
				0.6	B	25.9					
NANLOE*				0.7	B	10.5				14-atom	neg
				2.1	B	11.2				14-atom	3.4
PERPUY*	0.1	A	14.2							10-atom	15
	2.1	A	31.7							10-atom	14.7
	2.0	A	20.2							10-atom	15.9
							1.7	C	31.3	10-atom	20.7
QIBDAH*							0.8	C	29.9	10-atom	26.2
QIXVIC*	1.1	A	23.7							10-atom	10.1
							1.0	C	33	10-atom	10.6
RALFAM*				1.4	B	8.7					
				0.8	B	6.6					
REPNUV*	1.4	A	24.6								
RERWIV*				2.4	B	39.5					
							2.4	C	14.1		
SENYAM*							5.7	C	39.6****		
	2.2	A	29.2							14-atom	23.9
				1.9	B	22.2				14-atom	12.2
				0.7	B	14.9				14-atom	9.1
SEQBEW	0.4	A	0.5								
	1.1	A	8.3								
VAWDIH,***							2.1	A-C	29.9		
VERMIP*							4.3	C	32.2****		
							5.0	C	92.4****		
	1.4	A	30.4								
	2.5	A	16.2								
WEDVUX				0.5	B	12.1				17-atom	5.5
				1.0	B	9.3				17-atom	7
WEDWAE*,***	1.4	A	10.6							10-atom	neg
WEWDUY				1.2	B	26.4				10-atom	6.2
WEXCEI*							10.8	C	128****		
				1.8	B	13.6				14-atom	neg
XESRUJ*							1.4	C	24.6	10-atom	13.1
XIPGEM**							1.4	A-C	8.6	10-atom	neg
	3.0	A	36.2							10-atom	21
ZOJRAR01*				0.4	B	17				(D-W)	16.1

Table 7C Rigidity and $<\Phi^2>$ for CSD entries, by TBG type: Types **A**, **B** and **C**: Summary

average by type		34 A	20.2		35 B	12.6		19 C	17.8
total <F ²>			685.5			440.4			339.1
average deviation			7.5			7.2			7.4
minimum <F ²>			0.0			0.0			5.1
maximum <F ²>			36.9			39.5			33.0
CHNO average		27 A	20.6		18 B	14.5		14 C	19.2
total <F ²>			555.3			261.6			269.1
average deviation			6.7			8.1			7.0
minimum <F ²>			0.0			0.0			5.2
maximum <F ²>			36.2			39.5			33.0
CH average		7 A	15.8		0 B	0		8 C	13.7
total <F ²>			110.3			0			109.8
average deviation			11.7			0			3.4
minimum <F ²>			0.0			0			5.2
maximum <F ²>			36.2			0			18.9
CH, omit		3A	15.0		0 B	0		2 C	13.4
p-t-butylphenyl									
total <F ²>			45.1						26.7
average deviation			14.1						4.8
minimum <F ²>			1.3						8.6
maximum <F ²>			36.2						18.1

Table 9B. Bond length corrections (THMA14C) for 6 TBGs in this study. The contributions of ARG motion and overall molecular motion are shown. Distances in Å, angles in °.

C_t	C_{Me}	Distance	Corrected distance	Total correction	Correction, overall motion	ARG No.	ARG correction	Angle C_{Ar}-C_t-C_{Me}	$<F^2>$/ deg^2
III(a), Type **A**-**C**									
C29	C30	1.5335	1.546	0.0123	0.0018	1	0.0105	112.4 almost in plane	52
C29	C31	1.5374	1.551	0.0131	0.0021	1	0.0110	108.9	
C29	C32	1.5376	1.550	0.0123	0.0015	1	0.0108	110.7	
C33	C34	1.5360	1.542	0.0062	0.0019	2	0.0043	110.9	22
C33	C35	1.5448	1.551	0.0064	0.0019	2	0.0045	108.0	
C33	C36	1.5310	1.537	0.0055	0.0013	2	0.0042	112.2 almost in plane	
V(a), high resolution, Type **A**									
C31	C32	1.5332	1.552	0.0186	0.0009	2	0.0176	109.1	84
C31	C33	1.5263	1.544	0.0180	0.0012	2	0.0168	112.3 in plane	
C31	C34	1.5366	1.555	0.0184	0.0009	2	0.0175	109.8	
V(a), high resolution, no correlations, 2-ARG , Dunitz-White, Type **A**									
C27	C28	1.5346	1.539	0.0049	0.0009	1	0.0039	108.5	19
C27	C29	1.5392	1.544	0.0050	0.0011	1	0.0039	109.5	
C27	C30	1.5302	1.535	0.0045	0.0013	2	0.0031	112.5 in plane	16
VII(a), whole molecule Type **C**									
C27	C28	1.5323	1.542	0.0099	0.0008	1	0.0092	111.5	45
C27	C29	1.5314	1.541	0.0098	0.0006	1	0.0092	111.4	
C27	C30	1.5309	1.541	0.0100	0.0004	1	0.0096	107.8 perpendicular	
TMP, (B), whole molecule (Table 8), Type **B**									
C7'	C8'	1.5404	1.547	0.0066	0.0051	1	0.0015	109.8	7
C7'	C9'	1.5285	1.536	0.0076	0.0061	1	0.0015	112.1 in plane	
C7'	C10'	1.5369	1.544	0.0076	0.0061	1	0.0015	110.2	
TBBrX, no correlations, 2-ARG, Dunitz-White (Table 8), Type **A**									
C7	C8	1.5339	1.542	0.0081	0.0018	1	0.0063	109.3	30
C7	C9	1.5267	1.530	0.0038	0.0010	2	0.0028	112.1 in plane	14
C7	C10	1.5357	1.544	0.0080	0.0018	1	0.0063	109.1	(30)