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Synthesis of an Extremely Crowded Naphthalene via a Stable Norbornadienone

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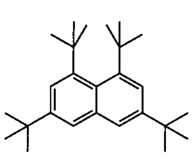
Abstract: Computational studies at the HF/3-21G and B3LYP/6-31G(d) levels suggest that 5,6,8-tri(*tert*-butyl)-1,2,3,4-tetraphenylnaphthalene (**2**) is perhaps the most crowded naphthalene derivative that will show normal stability; more highly congested naphthalenes will prefer to exist as the corresponding Dewar isomers. Initial attempts to prepare **2** by reacting 3,4,5,6-tetraphenylbenzyne with 2,3,5-tri(*tert*-butyl)cyclopentadienone at 83 °C gave instead a stable norbornadienone, 1,2,4-tri(*tert*-butyl)-5,6,7,8-tetraphenyl-9-oxo-1,4-dihydro-1,4-methanonaphthalene (**3**), which was characterized by X-ray crystallography. The experimental and calculated (HF/3-21G) activation energies (E_a) for the decarbonylation of **3** were quite high: 39 and 46 kcal/mol, respectively, a manifestation of the substantially increased strain in the transition state as the *tert*-butyl groups are forced together. The naphthalene **2** was obtained in good yield by heating **3** in refluxing toluene, and its X-ray structure showed exceptional distortions from a normal naphthalene geometry. However, **2** is not completely stable, and it decomposes upon prolonged heating in xylenes.

Introduction

Many octasubstituted naphthalenes have been prepared and structurally characterized, including a variety of octaaryl-,[1] octahalo-,[2] octakis(arylthio)-,[3] and octakis(aryloxy)naphthalenes,[4] as well as octamethylnaphthalene,[5] octapyrrolylnaphthalene,[6] and a few others with mixed substituents. The naphthalene cores of these molecules are significantly distorted from a normal, planar geometry, usually in the form of an end-to-end twist of 20−30°. However, tertiary butyl groups have much greater steric demands than any of the substituents listed above, and perhaps for this reason, only two crystal structures exist of naphthalene derivatives having more than two *tert*-butyl groups.[7,8] Of these, only 1,3,6,8-tetra(*tert*-butyl)naphthalene[7] (**1**) possesses significant steric crowding. We have a long-standing interest in highly distorted, polyphenyl polycyclic aromatic compounds,[1,9] and we wondered to what extent the phenyl groups in such molecules can be replaced by even bulkier *tert*-butyl groups without loss of stability under normal conditions.[10] In the present paper, we report the synthesis and structural characterization of the extremely crowded naphthalene **2**, its unusually stable norbornadiene precursor **3**, and the results of computational studies on these and related poly(*tert*-butyl)arenes.



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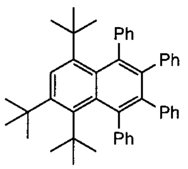

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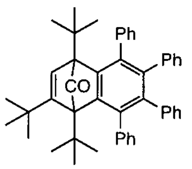

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Results and Discussion

Computational Studies of Poly(*tert*-butyl)arenes. At the outset of this project, we decided to use modern computational methods to judge which of several attractive, highly crowded naphthalenes might be reasonable synthetic targets. To assess the accuracy of such methods, the structures and energies of various isomers and conformers of four *known* poly(*tert*-butyl)arenes and related compounds were calculated: 1,2,3,4-tetra(*tert*-butyl)benzene (**4**, Table 1), hexakis(trimethylsilyl)benzene

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(10) An additional motivation for this work was the finding that decaphenylanthracene displays exceptionally stable electrogenerated chemiluminescence (ECL) (Debad, J. D.; Lee, S. K.; Qiao, X.; Pascal, R. A., Jr.; Bard, A. J. *Acta Chem. Scand.* **1998**, *52*, 45−50). Unfortunately, the synthesis of decaphenylanthracene proceeds in very low yield. Octaphenylnaphthalene is much more easily prepared, and it shows strong, but less persistent ECL. We hope that, by increasing the steric bulk of the substituents, it may be possible to improve the ECL performance of naphthalene derivatives while retaining easy synthetic access.

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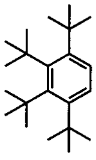
Table 1. Calculated Energies for Conformations and Isomers of Poly(*tert*-butyl)arenes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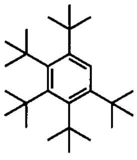
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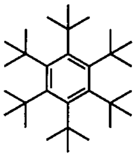
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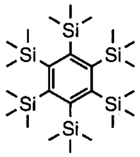

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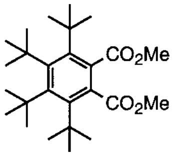

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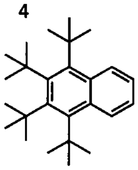
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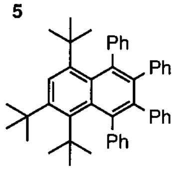

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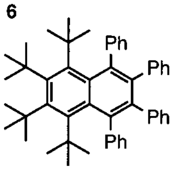

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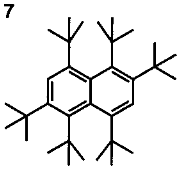
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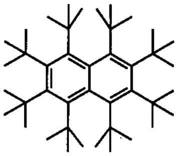
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		E (au) [Δ*E* (kcal/mol)] {no. of imaginary freq}					
cmpd	symm	HF/STO-3G		HF/3-21G(*)		B3LYP/6-31G(d)	
4	C_2	−845.008 595	[0.0] {0}	−850.382 754	[0.0]	−861.140 182	[0.0] {0}
4 Dewar	$C_1{}^a$	−844.979 472	[18.3] {0}	−850.323 377	[37.3]	−861.078 573	[38.7]
4 Dewar	$C_1{}^b$	−845.035 496	[−16.9] {0}	−850.376 020	[4.2]	−861.127 078	[8.2]
5	C_1	−999.267 931	[0.0] {0}	−1005.607 370	[0.0]	−1018.349 486	[0.0]
5 Dewar	$C_1{}^a$	−999.283 976	[−10.1] {0}	−1005.589 882	[11.0]	−1018.323 592	[16.2]
5 Dewar	$C_1{}^b$	−999.338 542	[−44.3] {0}	−1005.637 644	[−19.0]	−1018.369 458	[−12.5]
6	D_3	−1153.457 177	[0.0] {0}	−1160.772 516	[0.0]	−1175.504 814	[0.0] {0}
6	C_2	−1153.432 593	[15.4] {1}	−1160.744 474	[17.6]	−1175.485 363	[12.2] {0}
6	D_{3d}	−1153.398 537	[36.8] {6}	−1160.721 415	[32.1]	−1175.460 225	[28.0] {6}
6	S_6	−1153.404 370	[33.1] {5}	−1160.722 750	[31.2]	−1175.462 126	[26.8] {5}
6 Dewar	C_2	−1153.546 009	[−55.7] {0}	−1160.808 338	[−22.5]	−1175.527 495	[−14.2] {0}
7	D_3	−2643.127 268	[0.0] {0}	−2660.260 435	[0.0]	−2684.167 102	[0.0]
7 Dewar	C_2	−2643.164 818	[−23.6] {0}	−2660.239 622	[13.1]	−2684.145 892	[13.3]
8	C_2	−1292.311 704	[0.0] {0}	−1301.096 612	[0.0]	−1316.855 868	[0.0] {0}
8 Dewar	$C_1{}^a$	−1292.321 500	[−6.1] {0}	−1301.082 677	[8.7]	−1316.834 258	[13.6]
8 Dewar	$C_1{}^b$	−1292.368 342	[−35.5] {0}	1301.135 534	[−24.4]	−1316.872 282	[−10.3]
9 twist	C_2	−995.765 739	[0.0] {0}	−1002.146 536	[0.0]	−1014.753 158	[0.0] {0}
9 boat	C_1	nm[c]		−1002.115 579	[19.4]	−1014.727 347	[16.2]
9 Dewar	C_1	−995.791 570	[−16.2] {0}	−1002.140 944	[3.5]	−1014.736 363	[10.5]
2 twist	C_1	−1748.514 192	[0.0] {0}	−1759.978 434	[0.0]	−1781.746 944	[0.0]
2 boat	C_1	−1748.511 672	[1.6] {0}	−1759.975 974	[1.5]	−1781.745 322	[1.0]
2 Dewar	C_1	−1748.519 536	[−3.4] {0}	−1759.956 088	[14.0]	−1781.712 637	[21.5]
10 twist	C_2	−1902.708 083	[0.0] {0}	−1915.143 378	[0.0]		
10 boat	C_1	−1902.706 855	[0.8] {0}	−1915.142 014	[0.9]		
10 Dewar	C_1	−1902.783 073	[−47.1] {0}	−1915.182 650	[−24.6]		
11 twist	C_2	−1304.359 034	[0.0] {0}	−1312.658 940	[0.0]	−1329.224 398	[0.6]
11	C_i	−1304.351 314	[4.8] {0}	−1312.654 075	[3.1]	−1329.225 396	[0.0]
11 Dewar	C_1	−1304.363 255	[−2.6] {0}	−1312.633 590	[15.9]	−1329.193 492	[20.0]
12 twist	D_2	−1612.690 776	[14.9] {0}	−1622.935 775	[12.3]	−1643.493 857	[14.0]
12	C_i	−1612.709 106	[3.4] {1}	−1622.955 411	[0.0]	−1643.516 128	[0.0] {0}
12	C_1	−1612.714 510	[0.0] {0}	−1622.955 076	[0.2]	−1643.514 742	[0.9]
12 Dewar	C_1	−1612.776 938	[−39.2] {0}	−1622.979 634	[−15.2]	−1643.524 583	[−5.3]

[a] Two *tert*-butyl groups on bridgehead carbons. [b] One *tert*-butyl group on bridgehead. [c] Not a minimum.

(**7**), dimethyl 3,4,5,6-tetra(*tert*-butyl)phthalate (**8**), and 1,2,3,4-tetra(*tert*-butyl)naphthalene (**9**). Compounds **4**,[11] **7**,[12] and **9**[13] preferentially exist as ordinary arenes, but benzene **8** undergoes thermal isomerization to one of its Dewar isomers.[14] The Dewar isomers of **7** and **9** are also known but revert thermally to the arene, as expected.[12,13] To be useful, a computational method must reproduce the known relative stabilities of the valence isomers of these crowded arenes.

The results of computational studies at the HF/STO-3G, HF/3-21G(*),[15,16] and B3LYP/6-31G(d)[17−19] levels are given in Table 1. Analytical frequency calculations were performed for all structures at the HF/STO-3G level, as well as for selected structures (generally those optimized under symmetry constraints) at the B3LYP/6-31G(d) level. The HF/STO-3G calculations found that the Dewar isomers are more stable than the

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[16] The "(*)" designation applies only to the calculations for **7**; the 3-21G and 3-21G(*) basis sets are identical for compounds containing only first-row elements.[15]

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normal arenes *in every case*; therefore, this method is not reliable when dealing with this class of compounds. Fortunately, both the HF/3-21G(*) and B3LYP/6-31G(d) methods correctly predict the relative stabilities of the valence isomers of **4**, **7**, **8**, and **9**, and in addition, they give qualitatively identical rankings of the energies of the various benzene conformations and valence isomers examined. All three methods were then used to examine other, unknown, crowded benzenes and naphthalenes.

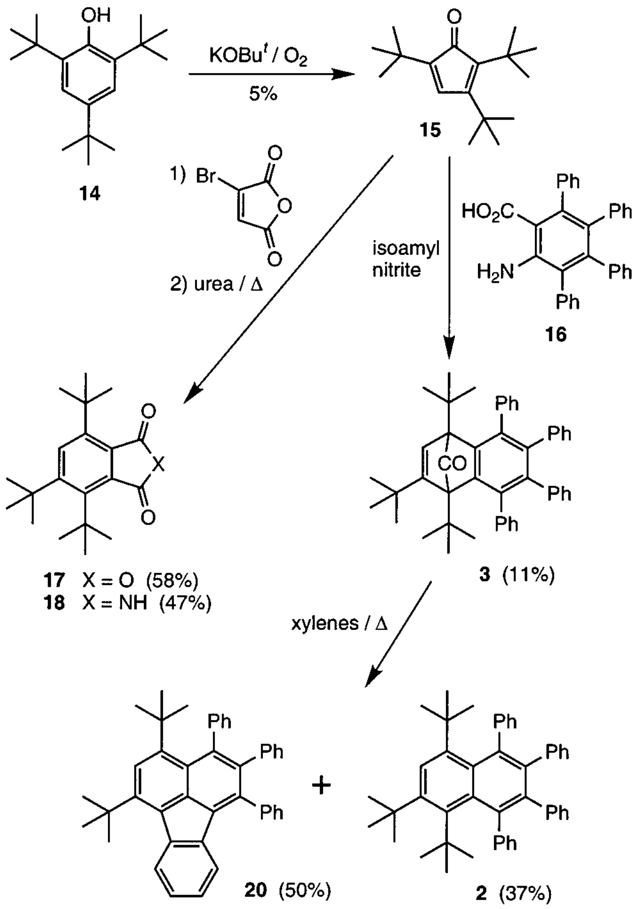
The Dewar isomers of penta(*tert*-butyl)benzene (**5**) and hexa(*tert*-butyl)benzene (**6**) are calculated to be substantially more stable than the normal arenes. The arenes are strongly distorted from planarity due to nonbonded conflicts between the peripheral *tert*-butyl groups, and much of this strain is relieved in the Dewar isomers. A previous computational study of **6** by Mislow and co-workers,[20] which employed the MM2 force field, found two minimums for the arene: a D_3-symmetric ground state and an S_6 conformation 18.4 kcal/mol higher in energy. The present calculations also find the D_3 conformation to be the arene ground state, but the S_6 conformation is not a potential minimum. Interestingly, at the B3LYP/6-31G(d) level, there is a second minimum with C_2 symmetry, but at the (less reliable) HF/STO-3G level, this conformation is a transition state.

The most appealing of the crowded naphthalenes that we had considered as targets for synthesis were 5,6,7,8-tetra(*tert*-butyl)-1,2,3,4-tetraphenylnaphthalene (**10**) and octa(*tert*-butyl)naphthalene (**12**). However, the Dewar isomers of both **10** and **12** are calculated to be more stable than the normal arenes, as might be expected in light of the computational results for **5** and **6**. We are more interested in the properties of distorted naphthalenes than Dewar naphthalenes,[10] so the removal of one or more of the substituents on **10** and **12** was indicated. Several possibilities were examined, but we judged 5,6,8-tri(*tert*-butyl)-1,2,3,4-tetraphenylnaphthalene (**2**) and 1,2,4,5,6,8-hexa(*tert*-butyl)naphthalene (**11**) to be synthetically most accessible. Both compounds are calculated to have naphthalene ground states, and interestingly, both have two minimums that are very close in energy. For **2**, the tri(*tert*-butyl)benzene ring may adopt either a twisted or a boat conformation, and the calculated difference in energy is 1.0 kcal/mol at the B3LYP/6-31G(d) level. For **11**, there exist dramatically different C_2 and C_i conformations with a calculated difference in energy of only 0.6 kcal/mol. If these compounds could be prepared and structurally characterized, they would provide a strong test of the accuracy of these computational methods.

Synthesis, Structure, and Decarbonylation of Norbornadiene 3. Naphthalenes **2** and **11** might be synthesized by the reactions of 3,4,5,6-tetraphenylbenzyne and 3,4,6-tri(*tert*-butyl)benzyne, respectively, with 2,3,5-tri(*tert*-butyl)cyclopentadienone (**15**). The former aryne is easily formed from known 3,4,5,6-tetraphenylanthranilic acid[1a] (**16**), and the latter would be generated similarly from 3,4,6-tri(*tert*-butyl)anthranilic acid, which itself might prepared from **15** in a few steps.

Scheme 1 illustrates the approaches in both syntheses. Compound **15** is easily prepared by oxygenation of 2,4,6-tri(*tert*-butyl)phenol in base.[21] In our hands, the yield is very low (5%), but the starting materials are inexpensive. Diels−Alder reaction of **15** with bromomaleic anhydride smoothly gives 3,4,6-tri(*tert*-butyl)phthalic anhydride (**17**), and heating the product with urea yields the imide **18**. Unfortunately, all attempts to convert **18** to the corresponding anthranilic acid, by Schmidt reaction or Hoffman degradation, under the conditions used to make **16**[1a] as well as under more stringent conditions, were unsuccessful. Given that **16** is readily available, we put aside the synthesis of **11** and concentrated on preparation of naphthalene **2**.

Scheme 1



Diazotization of **16** in refluxing 1,2-dichloroethane (83 °C) in the presence of **15** gave a low yield (11%) of an adduct having plausible ^{1}H NMR and mass spectra (*m/z* 600) for the desired naphthalene **2**. However, the ^{13}C NMR spectrum showed a carbonyl resonance (δ 192.6), two extra aliphatic resonances, and a deficiency of aromatic resonances. Careful crystallization of this material followed by X-ray analysis confirmed our suspicion that the adduct was in fact the norbornadienone **3**. The molecular structure of **3** is shown in Figure 1. Many of the C−C bond lengths in the norbornadienone core are unusually long, though not exceptionally so [C(1)−C(2), 1.583 (2) Å; C(1)−C(8A), 1.570 (3) Å; C(1)−C(9), 1.567 (2) Å; C(4)−C(4A), 1.560 (3) Å; C(4)−C(9), 1.540 (2) Å], and the bonds to the bridgehead *tert*-butyl groups are also long, as would be expected [C(1)−C(10), 1.569 (2) Å; C(4)−C(18), 1.565 (2) Å]. It is clear that **3** contains substantial strain, yet it is completely stable at room temperature.

Very few norbornadienones with even moderate stability are known, and a search of the Cambridge Structural Database found only one X-ray structure of such a molecule—the polycycle **19**.[22] The enhanced stability of both **3** and **19** can be attributed to two factors. First, both norbornadienones are surrounded by sterically demanding groups, and in the decarbonylation transition state (as well as in the product), these groups must be forced

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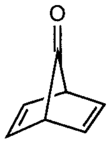
Table 2. Computational Data (HF/3-21G) for Norbornadienones and Their Decarbonylation Transition States (dts)



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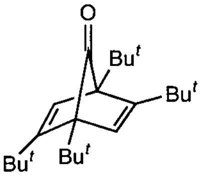

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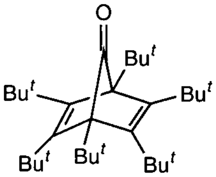

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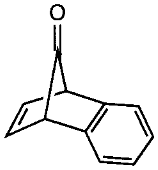

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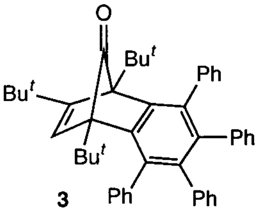


3

cmpd	symm	E (au)[a]	ZPE (au)[a]	E + ZPE	imag freq	ΔE (kcal/mol)	$\Delta E_{\mathrm{a(expt)}}$ (kcal/mol)
21	C_{2v}	−341.443 966	0.118 673	−341.325 293	0		
22	C_2	−962.533 990	0.603 882	−961.930 108	0		
23	C_2	−1272.882 585	0.852 389	−1272.030 196	0		
24	C_s	−493.265 565	0.170 269	−493.095 297	0		
3	C_1	−1872.094 393	0.881 841	−1871.212 552	0		
21 dts	C_{2v}	−341.410 383	0.115 414	−341.294 970	1	19.0	16 ± 2.5[b]
22 dts	C_2	−962.464 908	0.600 269	−961.864 640	1	41.1	17 ± 2[c]
23 dts	C_2	−1272.751 563	0.848 516	−1271.903 047	1	79.8	
24 dts	C_s	−493.220 179	0.166 459	−493.053 721	1	26.1	
3 dts	C_1	−1872.016 213	0.877 381	−1871.138 832	1	46.3	39.4 ± 1.5[d]

[a] 1 au = 627.503 kcal/mol. [b] Reference 24. [c] Reference 25. [d] This work.

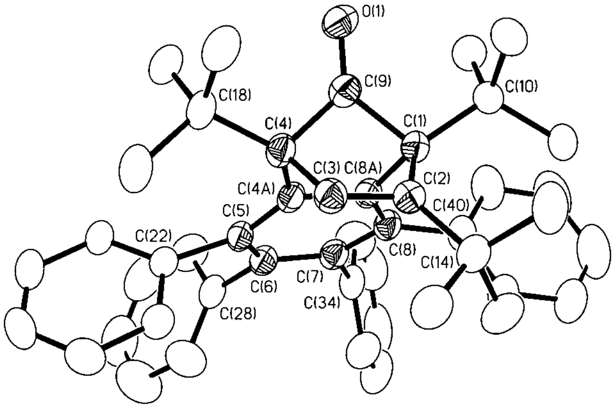
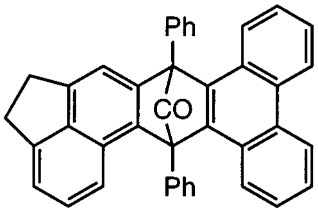


Figure 1. Molecular structure of norbornadienone **3**. Thermal ellipsoids have been drawn at the 50% probability level, and hydrogens have been omitted for clarity.

even more closely together. Second, fusion of the norbornadienone to aromatic rings lessens the thermodynamic driving force for the reaction (which is also felt in the transition state), since the product does not gain a full benzene ring's resonance stabilization upon expulsion of CO.



19

Both experimental and computational studies of the decarbonylation of **3** were performed. Our primary goal was the preparation of naphthalene **2**, so **3** was simply heated in refluxing xylenes (138 °C) for 12 h. This gave a 50% yield of **2** as well as a 37% yield of an unexpected product, the fluoranthene **20**, in which one of the *tert*-butyl groups of the starting material has been lost. Subsequently, it was found that heating **3** in refluxing toluene (110 °C) for 2 days gave almost exclusively naphthalene **2**. The formation of **20** will be discussed later in the context of the structure of **2**.

The kinetics of decarbonylation were determined by monitoring the ^{1}H NMR spectra of **3** in sealed tubes held at various temperatures. Relative concentrations of **3** and **2** were followed by integration of their characteristic *tert*-butyl resonances. The reaction was first order, with rate constants of $k_{373\mathrm{K}} = 3.7 \times 10^{-6}$ s^{-1}, $k_{393\mathrm{K}} = 5.8 \times 10^{-5}$ s^{-1}, and $k_{403\mathrm{K}} = 1.9 \times 10^{-4}$ s^{-1}. From these data, we calculate $E_a = 39.4 \pm 1.5$ kcal/mol, $\Delta H^{\ddagger}_{373} = 38.6 \pm 1.5$ kcal/mol, $\Delta S^{\ddagger}_{373} = 23 \pm 2$ cal/(mol·K), and $\Delta G^{\ddagger}_{373} = 30.1 \pm 1.5$ kcal/mol.

How do these data compare with the results of computational studies of decarbonylation? Birney et al.[23] examined the decarbonylation of norbornadienone itself (**21**, Table 2) by a variety of computational methods. HF/3-21G calculations of the energies of **21** and its decarbonylation transition state yielded results ($E_a = 19.0$ kcal/mol) in reasonable agreement with the existing experimental measurements ($E_a = 16 \pm 2.5$ kcal/mol,[24] $E_a = 17 \pm 2$ kcal/mol[25]). Fortunately, calculations at this level of theory are inexpensive enough to employ even on molecules as large as **3**.

We reproduced the result of Birney et al., and in addition, we located the decarbonylation transition states for 1,2,4,5-tetra(*tert*-butyl)norbornadienone (**22**), hexa(*tert*-butyl)norbnornadienone (**23**), benzonorbornadienone (**24**), and **3** (the last requiring a great deal of time due to its large size and low symmetry). These results are summarized in Table 2. The calculated barrier for decarbonylation of **3** is 46.3 kcal/mol, in fair agreement with experiment. Comparison of the data for **24** and **3** suggests that fusion of a benzene ring to the norbornadienone contributes no more than 7 kcal/mol of kinetic stabilization, but that steric crowding in the transition state raises the barrier to decarbonylation by as much as 20 kcal/mol in **3**.

The calculated decarbonylation transition state for **3** is shown in Figure 2. A comparison of Figures 1 and 2 shows that the C(1) and C(2) *tert*-butyl groups are forced more closely together as the reaction proceeds. Compound **3** is asymmetric and so is the transition state structure; the C(1)−C(9) and C(4)−C(9) bond distances are 2.168 and 2.085 Å, respectively. The average of

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(23) Birney, D. M.; Wiberg, K. B.; Berson, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6631−6642.

(24) Birney, D. M.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4553−4554.

(25) LeBlanc, B. F.; Sheridan, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4554−4556.

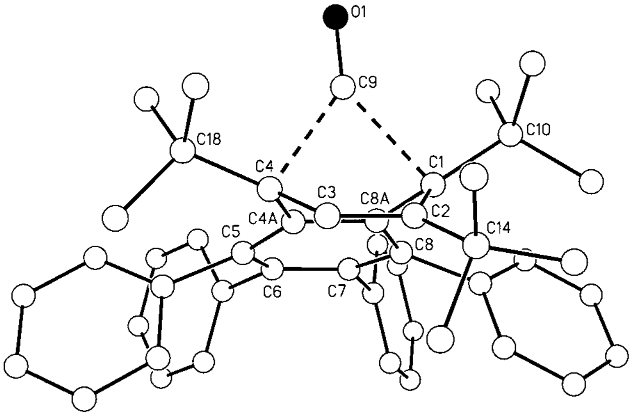
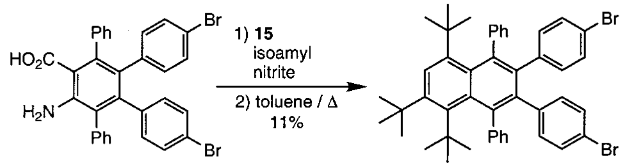


Figure 2. Transition state for the decarbonylation of norbornadienone **3** calculated at the HF/3-21G level. The crystallographic numbering scheme for **3** has been used to facilitate comparison with Figure 1.

these distances, 2.126 Å, suggests that this transition state is somewhat later than those calculated for **21** (1.985 Å), **24** (2.025 Å), and **22** (2.092 Å) but earlier than for **23** (2.291 Å) (all have symmetric transition states). As might be expected, the calculated activation energies increase with the increasing bond distances in the transition state. Finally, we note that both tetra- and hexa(*tert*-butyl)norbornadienone (**22** and **23**, respectively) should be stable at room temperature. Indeed, the calculated barrier for decarbonylation of **23** is so high (79.8 kcal/mol) that one suspects that some other reaction would occur instead.

Structure and Stability of Naphthalene 2. Naphthalene **2** was prepared as described above. However, it proved very difficult to grow satisfactory single crystals for X-ray diffraction. Our prior calculations had suggested that **2** might possess two low-energy conformations (Table 1), a situation that sometimes confounds crystallization experiments because the sample is effectively “impure”, but the ^{13}C NMR spectrum of **2** indicated that if this is the case, then the conformers are in relatively rapid equilibrium. We therefore decided to prepare a simple derivative of **2**, in the hope that it would crystallize more easily. A sample of the brominated anthranilic acid **25** was available,[26] so this



25 **26**

was converted to the corresponding naphthalene **26**.

Compound **26** gave excellent crystals from ethanol, and its X-ray structure was determined. As so often seems to be the case, once this structure was in hand, **2** crystallized, and its X-ray structure was also determined. (The structures are not related, so this is not likely to be a case of inadvertent seeding.) The molecular structures of the two crystallographically independent molecules of **2** are shown in Figure 3, and the molecular structure of **26** is shown in Figure 4. In addition, the X-ray structure of the byproduct fluoranthene **20** was also determined, and this is illustrated in Figure 5.

The tri(*tert*-butyl)tetraphenylnaphthalenes **2** and **26** are severely distorted from planarity, and these distortions are for the most part well-reproduced by the HF/3-21G and B3LYP/6-31G(d) calculations. Earlier we noted that both calculations showed a 1 kcal/mol preference for a twisted conformation of **2** rather than one in which the rings adopt boat conformations (Table 1); the experimental structures confirm this prediction. Specific distortions for **26** are discussed below, and the B3LYP/6-31G(d) values for the same parameters are in brackets. (The X-ray structures of **2** and **26** are very similar, but the quality of the determination for **26** is much superior, so its metrical parameters will be used for most of this discussion.)

Compound **26** displays an overall 29.5° end-to-end twist of the naphthalene core, but it is the conflict of the C(4) phenyl and the C(5) and C(6) *tert*-butyl groups that is most acute. This results in a significant pyramidalization of C(5), which is 0.128 Å [0.132 Å] above the plane defined by C(4A), C(6), and C(33). The torsion angle C(4)−C(4A)−C(5)−C(33) is 53.9° [54.8°], much greater than the value of 42° for the same angle in **1**.[7] Furthermore, all three naphthalene−(*tert*-butyl) bonds are stretched in **26**: C(5)−C(33), 1.578 (4) Å [1.585 Å]; C(6)−C(37), 1.563 (4) Å [1.572 Å]; C(8)−C(41), 1.563 (4) Å [1.565 Å]. For comparison, the naphthalene−(*tert*-butyl) bonds in **1** at C(1) and C(8) are 1.557 Å and at C(3) and C(6) average 1.524 Å.

The large distortions in **2** and **26** are suggest that they might not be thermally stable. We were intrigued by the fact that decarbonylation of the precursor **3** at 110 °C gave predominantly **2**, but that decarbonylation at 138 °C gave both **2** and the fluoranthene **20**, and we hypothesized that **20** is a decomposition product of **2**. Figure 4 has been drawn to facilitate comparison of **26** with the structure of **20** (Figure 5). It is clear that C(32) of the C(4) phenyl group is poised to interact with the already-pyramidalized C(5) carbon. The observed C(32)−C(5) distances are 3.122, 3.153, (**2**, molecules A and B), and 3.581 Å (**26**); the B3LYP/6-31G(d) calculated distance is 3.186 Å. A fragmentation of the C(5)−C(33) bond might be expected to lead to C(5)−C(32) bond formation followed by **20** itself, which is nearly flat and essentially unstrained in comparison to **2**.

In fact, **2** is not a precursor for **20**. Although naphthalene **2** is not stable in refluxing xylenes (138 °C), decomposing with a half-life of roughly 1 day at this temperature, repeated thermolyses failed to show any of **20** in the rather complex mixture of decomposition products. These products contain new *tert*-butyl and olefinic resonances, as well as complex aromatic signals, but they have not been individually purified and characterized.

The fluoranthene **20** appears only in reactions in which **3** is present as starting material and must be formed by a second decomposition pathway of **3** which becomes competitive with ordinary decarbonylation at higher temperatures. The same sorts of intramolecular interactions observed in **2** are also seen in **3**, and homolysis of either C(1)−C(9) or C(1)−C(10) (see Figure 1), rather than a concerted decarbonylation, followed by attack of the nearby phenyl group, might yield **20**.

Conclusion

Compound **3** is only the second norbornadienone derivative to have been crystallographically characterized, and it is one of only a handful of relatively stable norbornadienones that have been reported.[22,27] No stable norbornadienone has been reported that lacks groups conjugated to one or both of the double bonds, but HF/3-21G calculations indicate that poly(*tert*-butyl)norbornadienones with at least four *tert*-butyl groups should be stable

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[26] Tong, L., Ph.D. Dissertation, Princeton University, 1998.

[27] (a) Meinwald, J.; Miller, E. G. *Tetrahedron Lett.* **1961**, 253−258. (b) Irie, T.; Tanida, H. *J. Org. Chem.* **1979**, *44*, 1002−1003. (c) Warrener, R. N.; Russell, R. A.; Pitt, I. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1675−1676. (d) Plater, M. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1991**, 317−321. (e) Miki, S.; Kagawa, H.; Matsuo, K.; Kobayashi, O.; Yoshida, M.; Yoshida, Z. *Tetrahedron* **1992**, *48*, 1567−1572.

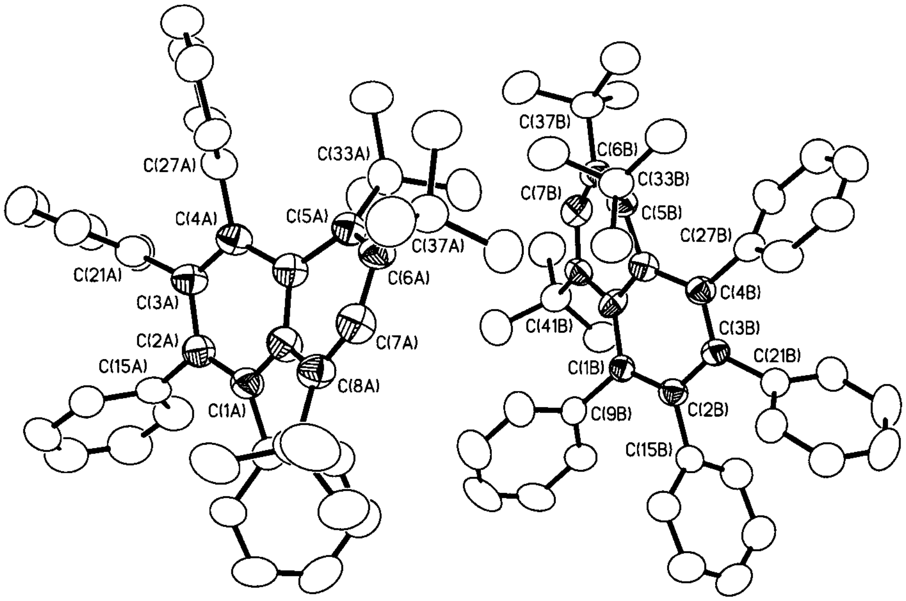

Figure 3. Molecular structure of naphthalene **2**. Both of the two crystallographically independent molecules are illustrated. Thermal ellipsoids have been drawn at the 50% probability level, and hydrogens have been omitted for clarity.

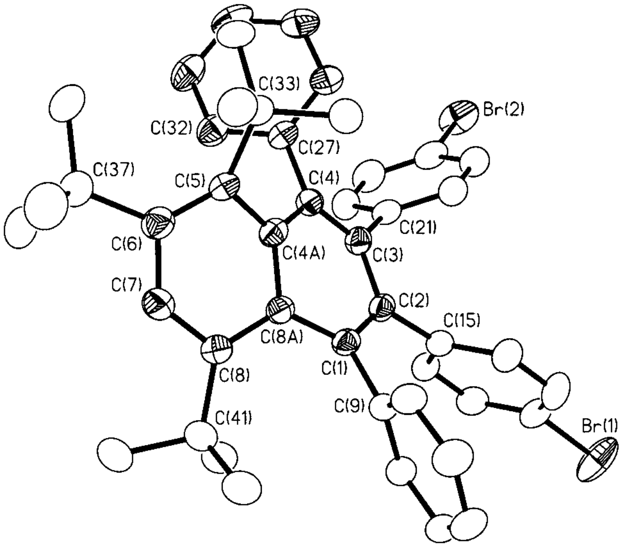

Figure 4. Molecular structure of naphthalene **26**. Thermal ellipsoids have been drawn at the 50% probability level, and hydrogens have been omitted for clarity. The molecule has been oriented to emphasize its relationship to **20** (Figure 5), and the carbon atoms that correspond to the fluoranthene nucleus of **20** have been shaded.

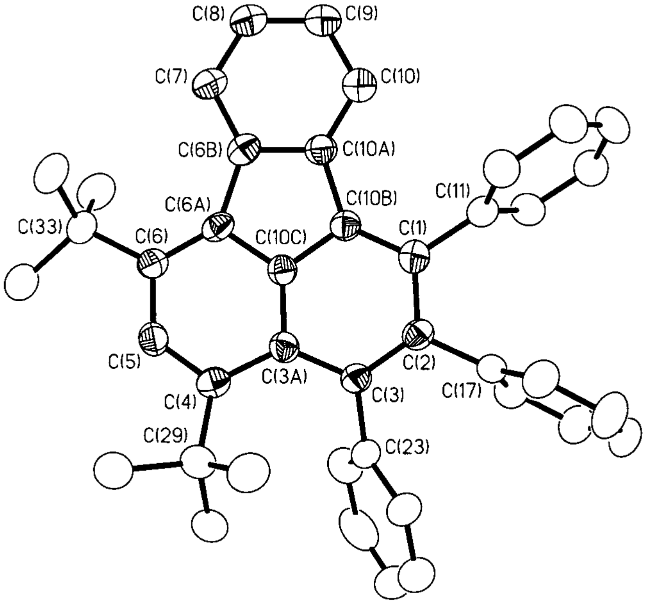

Figure 5. Molecular structure of fluoranthene **20**. Thermal ellipsoids have been drawn at the 50% probability level, and hydrogens have been omitted for clarity.

at room temperature (Table 2). It is important to note that such calculations give good models for the structure of **3** and the energetics of its decarbonylation reaction, the structure of the product naphthalene **2**, and the relative stabilities of known crowded benzenes and their Dewar isomers (Tables 1 and 2). Both HF/3-21G and B3LYP/6-31G(d) calculations indicate that **2** must be among the most crowded naphthalenes that can be made and remain stable under normal conditions. However, the distortions from a "normal" geometry in **2** are not as great as those observed in several of our most highly twisted polyphenyl polycyclic aromatic compounds, all of which have high thermal stability.[1,9] The fact that **2** does decompose upon moderate heating suggests that the presence of the *tert*-butyl groups facilitates some thermal decomposition pathway(s) and that poly(*tert*-butyl)arenes, unlike polyphenylarenes, are not be the best choice for applications where high stability is required.[10]

Experimental Section

3,4,5,6-Tetraphenylanthranilic acid (**16**) was prepared as previously described.[1a] 4,5-Bis(*p*-bromophenyl)-3,6-diphenylanthranilic acid (**25**) was a gift from Dr. Ling Tong.[26]

2,3,5-Tri(*tert*-butyl)cyclopentadienone (15). Potassium (48 g, 1.2 mol) was dissolved in *tert*-butyl alcohol (3 L). 2,4,6-Tri(*tert*-butyl)phenol (62.4 g, 0.238 mol) was then added, and after the phenol had completely dissolved, a gentle stream of oxygen was bubbled into the solution and it was heated at 60 °C for 6 h. The resulting red solution was poured into ice water, and the mixture was adjusted to pH 7 with 1 N HCl. The mixture was extracted twice with ether, and the combined extracts were washed with water and dried over Na_2SO_4. The solvent was removed to leave a dark brown residue (65.7 g). This material was redissolved in hexanes, and upon standing overnight, large, clear crystals were deposited (51.6 g). The deep orange mother liquor was fractionated on a silica gel column (hexanes). The first bright orange band to elute proved to be **15**, and this was set aside. Potassium (11.7

g, 0.30 mol) was dissolved in *tert*-butyl alcohol (1 L). The clear crystals collected previously were added, and the reaction mixture was heated under argon at 40 °C until its color turned dark red. Workup and column chromatography as before yielded a second fraction of **15**. The combined fractions containing **15** were concentrated to dryness, and the bright red-orange oil soon crystallized to give pure **15** (2.76 g, 11.1 mmol, 4.7%): mp 53.5−54 °C (lit.[21] 53−53.5 °C); ^{1}H NMR ($CDCl_3$) δ 1.13 (s, 9 H), 1.307 (s, 9 H), 1.311 (s, 9 H), 6.66 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.4, 31.6, 31.8, 32.6, 33.2, 33.9, 132.5, 138.8, 140.6, 156.9, 205.5 (11 of 11 expected resonances); MS (EI) *m/z* 248 (M$^+$, 27), 192 (M − C_4H_8, 46), 177 (M − CH_3 − C_4H_8, 100).

3,4,6-Tri(*tert*-butyl)phthalic Anhydride (17). A mixture of **15** (1.00 g, 4.0 mmol), bromomaleic anhydride (1.07 g, 6.0 mmol), and bromobenzene (3 mL) was heated to reflux under argon for 2 h. After cooling, most of the bromobenzene was removed by vacuum distillation, and the residue was fractionated on a silica gel column (16:1 hexanes−ethyl acetate) to give crude **17** as a yellow oil (0.91 g). Crystallization from hexanes−EtOAc gave colorless **17** (0.73 g, 2.3 mmol, 58%): mp 111.5−113 °C; ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 9 H), 1.52 (s, 9 H), 1.61 (s, 9 H), 7.83 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.8, 33.0, 34.1, 35.2, 38.9, 40.8, 126.5, 133.9, 135.0, 147.2, 153.1, 161.9, 162.9, 163.9 (14 of 14 expected resonances); MS (EI) *m/z* 316 (M$^+$, 41), 301 (M − CH_3, 100), 259 (M − C_4H_9, 39); exact mass 316.2027, calcd for $C_{20}H_{28}O_3$ 316.2038.

3,4,6-Tri(*tert*-butyl)phthalimide (18). Compound **17** (0.73 g, 2.3 mmol) and finely groud urea (10 g) were placed in a 250-mL round-bottom flask fitted with an air condenser. The mixture was heated to 170 °C for 36 h; periodically, sublimed urea was returned to the flask. After cooling, water (100 mL) was added to dissolve the unreacted urea, and the resulting mixture was extracted three times with chloroform. The combined extracts were washed with water and dried over Na_2SO_4. The solvent was evaporated, and the residue was recrystallized from chloroform−ethanol to give colorless **18** (343 mg, 1.09 mmol, 47%): mp 137−139 °C; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 9 H), 1.50 (s, 9 H), 1.60 (s, 9 H), 7.70 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.8, 33.5, 34.0, 34.8, 38.5, 40.2, 127.4, 133.1, 135.2, 145.5, 151.3, 159.4, 168.0, 169.7 (14 of 14 expected resonances); MS (EI) *m/z* 315 (M$^+$, 14), 300 (M − CH_3, 43), 258 (M − C_4H_9, 41), 244 (100); exact mass 315.2200, calcd for $C_{20}H_{29}NO_2$ 315.2198.

1,2,4-Tri(*tert*-butyl)-5,6,7,8-tetraphenyl-9-oxo-1,4-dihydro-1,4-methanonaphthalene (3). Compound **15** (0.25 g, 1.0 mmol) was dissolved in 1,2-dichloroethane (15 mL), and the solution was heated to reflux. Isoamyl nitrite (0.67 mL, 5.0 mmol) was added, followed by the slow addition of a solution of 3,4,5,6-tetraphenylanthranilic acid (0.28 g, 0.63 mmol) in 1,2-dichloroethane (50 mL) over 30 min. After heating for another hour, ethanol (12 mL) and 1% NaOH (36 mL) were added to quench the reaction. The reaction mixture was extracted with chloroform, the extract was washed with saturated $NaHCO_3$, and it was dried over Na_2SO_4. Removal of the solvent left 0.64 g of material, and this was fractionated by silica gel column chromatography (4:1 hexanes−benzene). The first component to elute was unreacted **15**, the second was 1,2,3,4-tetraphenylbenzene (R_f 0.40, 4:1 hexanes−benzene), and the third was **3** (71 mg, 0.113 mmol, 11%; R_f 0.32): ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 9 H), 1.20 (s, 9 H), 1.31 (s, 9 H), 5.23 (s, 1 H), 6.78−6.92 (m, 10 H), 7.08−7.17 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 26.6, 28.3, 30.0, 32.0, 36.2, 37.8, 40.1, 53.7, 125.9, 126.5, 127.0, 127.2, 127.3, 127.7, 127.8, 128.0, 129.7, 130.0, 130.2, 130.3, 130.7, 131.3, 131.6, 131.8, 133.7, 140.2, 140.6, 141.2, 142.1, 158.7, 192.6 (31 of 33 expected resonances); MS (EI) *m/z* 600 (M − CO, 4), 544 (M − CO − C_4H_8, 13), 487 (M − CO − C_4H_8 - C_4H_9, 19), 431 (M − CO − 2C_4H_8 − C_4H_9, 100). Single crystals of **3** were obtained from chloroform−methanol−ethylene glycol.

5,6,8-Tri(*tert*-butyl)-1,2,3,4-tetraphenylnaphthalene (2) and 4,6-Di(*tert*-butyl)-1,2,3-triphenylfluoranthene (20). Freshly purified **3** (25 mg, 0.040 mmol) was dissolved in xylenes (5 mL), and the solution was heated at reflux for 12 h. The solvent was evaporated to leave a yellow residue which was fractionated by preparative silica gel TLC (8:1 hexanes−benzene) to give two major components. The material with R_f 0.41 proved to be the naphthalene **2** (12 mg, 0.020 mmol, 50%): mp 155.0−155.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.80 (s, 9 H), 0.90 (s, 9 H), 1.49 (s, 9 H), 6.06 (br s, 1 H), 6.21 (d, J = 7.5 Hz, 1 H), 6.60 (br s, 1 H), 6.62 (t, J = 7.5 Hz, 1 H), 6.72−7.08 (m, 16 H), 7.42 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 33.1, 33.8, 34.4, 36.8, 39.7, 40.8, 125.0, 125.1, 126.0, 126.1, 126.3, 126.4, 126.6, 126.8, 127.3 (br), 130.5 (br), 130.7, 131.6, 132.0, 132.8, 133.0, 133.4 (br), 134.0 (br), 134.2, 135.6, 135.7, 136.2, 137.5, 139.5, 141.37, 141.42, 141.8, 144.7, 144.8, 145.0, 150.2 (36 resonances observed; 32 resonances are expected in the fast exchange limit, but 40 are possible if there is restricted phenyl rotation, as is evident from the broadened aryl resonances); MS (EI) *m/z* 600 (M$^+$, 7), 543 (M − C_4H_9, 13), 487 (M − C_4H_8 − C_4H_9, 26), 431 (M − 2C_4H_8 − C_4H_9, 100); exact mass 600.3774, calcd for $C_{46}H_{48}$ 600.3758. Single crystals of **2** were obtained upon solidification of the neat oil after the final step of the purification.

The material with R_f 0.32 proved to be the fluoranthene **20** (8 mg, 0.015 mmol, 37%): mp 246.5−247.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9 H), 1.76 (s, 9 H), 6.45 (d, J = 7 Hz, 1 H), 6.66 (m, 2 H), 6.86 (m, 3 H), 6.92 (m, 3 H), 7.02 (m, 3 H), 7.11 (m, 2 H), 7.21 (m, 2 H), 7.94 (s, 1 H), 8.19 (d, J = 8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 31.2, 33.6, 36.1, 37.7, 123.6, 125.4, 126.0, 126.42, 126.47, 126.6, 126.7, 126.9, 127.3, 128.0, 128.8, 129.1, 130.1, 131.3, 131.6, 133.2, 133.7, 135.7, 136.0, 138.2, 138.5, 140.0, 140.1, 140.4, 141.6, 144.0, 147.2, 150.2 (32 of 32 expected resonances); MS (EI) *m/z* 542 (M$^+$, 37), 471 (23), 429 (20), 105 (100); exact mass 542.2969, calcd for $C_{42}H_{38}$ 542.2975. Single crystals of **20** were obtained from dichloromethane−methanol.

When refluxing toluene was employed as the solvent for the decomposition of the norbornadienone **3**, the yield of the naphthalene **2** was nearly quantitative.

5,6,8-Tri(*tert*-butyl)-2,3-bis(4-bromophenyl)-1,4-diphenylnaphthalene (26). The synthesis of **26** was essentially the same as that of **2**. Compound **15** (0.40 g, 1.6 mmol) was dissolved in 1,2-dichloroethane (24 mL), and the solution was heated to reflux. Isoamyl nitrite (1.00 mL, 7.5 mmol) was added, followed by the slow addition of a solution of 4,5-bis(*p*-bromophenyl)-3,6-diphenylanthranilic acid (**25**, 0.97 g, 1.6 mmol) in 1,2-dichloroethane (80 mL) over 30 min. After heating for another hour, ethanol (18 mL) and 1% NaOH (54 mL) were added to quench the reaction. The reaction mixture was extracted with chloroform, the extract was washed with saturated $NaHCO_3$, and it was dried over Na_2SO_4. The solvent was removed, and the residue was fractionated by silica gel column chromatography (8:1 hexanes−benzene) to yield the norbornadienone intermediate (R_f 0.26, 8:1 hexanes−benzene), which was not characterized. This material was dissolved in toluene (10 mL), and the solution was heated at reflux for 24 h. Removal of the solvent left pure **26** (134 mg, 0.177 mmol, 11%): mp 204−205 °C; ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 9 H), 0.88 (s, 9 H), 1.48 (s, 9 H), 5.98 (br s, 1 H), 6.14 (dd, J = 8 Hz, 2 Hz, 1 H), 6.76 (dd, J = 8 Hz, 2 Hz, 1 H), 6.77 (br d, J = 8 Hz, 1 H), 6.78−7.18 (m, 14 H), 7.50 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 33.0, 33.8, 34.3, 36.9, 39.8, 40.8, 119.5, 119.6, 126.4, 126.5, 126.8, 127.0 (br), 127.1, 127.6 (br), 129.7, 129.8 (br), 130.1, 130.2 (br), 131.1, 132.2 (br), 132.9, 133.0, 133.1, 133.3 (br), 133.5, 133.9 (br), 134.1, 134.5 (br), 135.8, 135.9, 136.5, 139.6, 140.2, 140.3, 141.9, 144.1, 144.3, 145.2, 150.6 (39 resonances observed; 32 resonances are expected in the fast exchange limit, but 40 are possible if there is restricted aryl group rotation, as is evident from the broadened aryl resonances); MS (EI) *m/z* 758 (M$^+$, 37), 701 (M − C_4H_9, 35), 645 (M − C_4H_8 − C_4H_9, 100), 589 (M − 2C_4H_8 − C_4H_9, 96), 510 (78); exact mass 758.1922, calcd for $C_{46}H_{46}Br_2$ 758.1948. Single crystals of **26** were obtained from ethanol.

General X-ray Crystallographic Procedures. X-ray data were collected by using graphite-monochromated Mo Kα radiation (0.710 73 Å) on a Nonius KappaCCD diffractometer. The diffraction data were processed by using the program DENZO.[28] All structures were solved by direct methods using Siemens SHELXTL,[29] and all were refined by full-matrix least squares on F^2 using SHELXTL. All non-hydrogen atoms were refined anisotropically, and hydrogens were included with a riding model. The structure of **20** contain a highly disordered dichloromethane of crystallization; for this reason, the SQUEEZE/

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Table 3. Crystallographic Data for Compounds **2**, **3**, **20**, and **26**

	3	**20**	**2**	**26**
chemical formula	$C_{47}H_{48}O$	$C_{42}H_{38}\cdot CH_2Cl_2$	$C_{46}H_{48}$	$C_{46}H_{46}Br_2$
formula weight	628.85	627.65	600.84	758.65
crystal size (mm)	0.25 × 0.16 × 0.12	0.30 × 0.10 × 0.08	0.19 × 0.19 × 0.07	0.25 × 0.24 × 0.16
space group	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	22.8785 (5)	13.3467 (9)	10.1358 (9)	13.7798 (4)
b, Å	12.4546 (3)	9.3553 (5)	16.575 (1)	10.6379 (3)
c, Å	25.6155 (5)	27.408 (2)	22.172 (2)	27.2058 (9)
α, deg	90	90	76.860 (4)	90
β, deg	93.510 (1)	102.452 (2)	82.762 (4)	104.034 (1)
γ, deg	90	90	75.525 (4)	90
V, Å^3	7285.3 (3)	3341.7 (4)	3502.7 (5)	3869.0 (2)
Z	8	4	4	4
ρ_{calcd}, g/cm^3	1.147	1.248	1.139	1.302
μ, mm^{-1}	0.066	0.22	0.064	2.125
$F(000)$	2704	1328	1296	1568
T, K	200 (2)	200 (2)	200 (2)	200 (2)
$\theta_{\max}$, deg	25.0	22.5	22.5	27.5
reflections				
total	23848	20880	16721	35580
unique	6408	4325	9033	8853
obsd [$I > 2\sigma(I)$]	4347	2594	4215	3869
parameters	442	385	847	442
$R(F)$ (obs data)[a]	0.050	0.058	0.094	0.049
$wR(F^2)$ (obs data)[a]	0.112	0.137	0.133	0.100
S (obs data)[a]	1.11	1.14	1.26	1.08
$R(F)$ (all data)[a]	0.086	0.106	0.217	0.079
$wR(F^2)$ (all data)[a]	0.128	0.154	0.171	0.113
S (all data)[a]	1.03	0.97	1.05	1.02

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; S = goodness of fit on $F^2 = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

BYPASS procedure[30] implemented in PLATON-96[31] was employed to account for the disordered solvent electron density. Specific crystal, reflection, and refinement data are contained in Table 3, and full details are provided in the Supporting Information.

Computational Studies. All ab initio (HF/STO-3G, HF/3-21G[15]), and hybrid density functional [B3LYP/6-31G(d)[17−19]] calculations were performed by using GAUSSIAN 94 or GAUSSIAN 98;[32] the built-in default thresholds for wave function and gradient convergence were employed. When experimental and calculated structures were compared, the function OFIT in Siemens SHELXTL was used to determine the best fit of the experimental and calculated geometries and the deviations of the atomic positions.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for **2**, **3**, **15**, **17**, **18**, **20**, and **26**. A crystallographic information file (CIF), containing the full X-ray structural data for **2**, **3**, **20**, and **26**, and an ASCII text file, containing the atomic coordinates of the calculated structures of the arenes, norbornadienones, and transition states in Tables 1 and 2. This material is available free of charge at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

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