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# The Structure of 1,3,6,8-Tetra-*tert*-butylnaphthalene

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Abstract: The detailed molecular structure of a *peri*-di-*tert*-butylnaphthalene has been determined by x-ray crystallography and molecular mechanics calculation. Both methods describe a highly distorted nonplanar framework, a result which serves to confirm previous structural assumptions that were based on other spectroscopic techniques.

Highly congested molecules always present challenges to chemists. There is the synthesists' problem of trying to prepare such molecules and there is the theoreticians' goal of trying to predict or interpret why the structures and properties come out the way they do. Both the 1,8-dimethylnaphthalene **1** and the *o*-di-*tert*-butylbenzene system **2** have been subjects

1   **2**
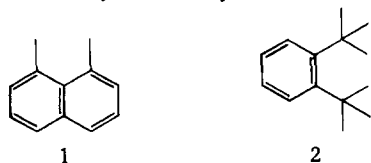
of molecular mechanics calculations and x-ray crystallography.[2,3] In both molecules, the methyl groups are closer than permitted by the sum of van der Waals radii and hence the molecules are strained. In both systems, the adjustment to the strain was observed experimentally as an outward in-plane bending of substituent groups. The major adjustment of the aromatic ring was bond angle deformation, but there was no significant deviation from planarity. When the methyl groups of 1,8-dimethylnaphthalene are replaced with *tert*-butyl groups, the congestion is much more severe. The successful synthesis of such compounds[4] was an invitation to molecular mechanics methodology[3b,5] to determine the structure of the system, particularly since the x-ray crystallographic study had not been completed when the calculations were done. Now that the x-ray work has been concluded, we wish to report both the calculated and experimental structures of the 1,8-*peri-tert*-butylnaphthalene system, specifically, the tetra-*tert*-butylnaphthalene **3**.

3   **4**
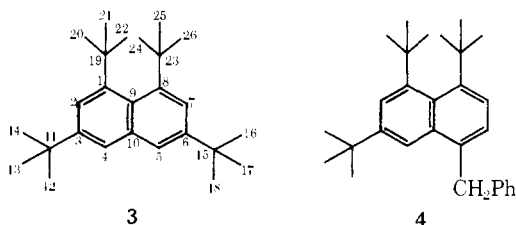
Experimental Section

X-Ray Analysis. The crystals are triclinic with $a = 9.886$ (3), $b = 10.437$ (3), $c = 12.125$ (4) Å, $\alpha = 82.48$ (3), $\beta = 85.63$ (3), $\gamma = 71.32$

(3)°, $V = 1170$ Å^3. The space group is $P\bar{1}$ with two molecules per cell, $D_c = 0.999$ g cm^{-3}, μ (Cu Kα radiation) = 4.11 cm^{-1}.

Intensity data were collected on an Enraf-Nonius CAD 4 diffractometer, using monochromatized Cu Kα radiation, up to a limit of $\theta = 75°$. The $\omega - 2\theta$ scanning mode was used and reflections were accepted as observed on the criterion $I/\sigma I > 3$. Complete data were collected from two separate crystals, a small one approximately cube shaped with edge 0.2 mm, and a much larger crystal, roughly spherical and with mean diameter 0.67 mm. A total of 4452 independent reflections, or 89% of those possible, was accepted. Initial work was done using the large crystal data, but after structure solution and isotropic refinement, the two sets were combined by a least-squares fit of the scales, at the same time subtracting out the differential spherical absorption between the two crystals. Some extinction was evident in the low angle data from the large crystal. Therefore data from the small crystal only were used for the range sin $\theta/\lambda < 0.325$ Å^{-1}. This reduced the data to 4027 reflections giving a data/parameter ratio of 10.2 in the final refinement. Data reduction was carried out via NRC program 02.[6]

The E statistics favored a centrosymmetric structure and this was strengthened by the results of the ORNL search program ORTRAN.[7] A 12-atom moiety consisting of the naphthalene ring and the two presumably coplanar first substituent atoms in the 3,6 positions was used and only one independent orientation was found. In order to determine the translation, this fragment was placed in an arbitrary position of the space group $P1$ and atoms added in from successive electron density maps (NRC program 08[8]) until this molecule was complete. The second molecule then appeared related by a center of symmetry to the first. Coordinates were then transformed to this center as origin and refinement carried out in the space group $P1$. Full-matrix least-squares refinement of the carbon atom parameters was carried out on a CDC 6600 computer using the ORNL program ORXFLS3.[9] Two cycles with isotropic thermal parameters reduced R to 0.158, and two subsequent cycles using anisotropic thermal parameters gave an R of 0.096. The hydrogen atoms were then located using a modified FORDAP (BNL)[10] program. Subsequent refinement (anisotropic carbon atoms, isotropic hydrogen atoms) gave a final R value 0.057 and wR of 0.058 for all observed reflections. The weighting scheme used was based on the counting statistics and the function minimized in least-squares refinement was $\Sigma w(F_o - KF_c)^2$. The form factors used are those given in the International Tables.[11] The observed and calculated structure factors are found in Table I (microfilm edition). The structural parameters for all atoms are given in Table II. Bond distances and bond angles are found in Table III.

Molecular Mechanics Calculations. The conclusions here were arrived at simultaneously with and independently from the x-ray work. The previously described force field (MMPI-1973) was used.[3b,5]

Table II. Coordinates and Thermal Parameters for All Atoms[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C1	−0.1516 (2)	0.0231 (2)	−0.2134 (1)	76 (2)	91 (2)	65 (1)	−22 (1)	−5 (1)	−22 (1)
C2	−0.2472 (2)	0.1170 (2)	−0.1522 (1)	91 (2)	89 (2)	71 (1)	−30 (1)	−7 (1)	−25 (1)
C3	−0.3954 (2)	0.1342 (1)	−0.1394 (1)	82 (2)	68 (1)	60 (1)	−12 (1)	−4 (1)	−12 (1)
C4	−0.4455 (2)	0.0594 (2)	−0.2004 (1)	73 (1)	74 (1)	59 (1)	−12 (1)	−3 (1)	−11 (1)
C5	−0.4119 (2)	−0.1153 (2)	−0.3243 (1)	74 (2)	78 (1)	63 (1)	−22 (1)	−7 (1)	−14 (1)
C6	−0.3282 (2)	−0.2188 (2)	−0.3806 (1)	88 (2)	78 (1)	58 (1)	−28 (1)	−4 (1)	−13 (1)
C7	−0.1822 (2)	−0.2695 (2)	−0.3527 (1)	89 (2)	83 (1)	68 (1)	−11 (1)	−6 (1)	−24 (1)
C8	−0.1199 (2)	−0.2131 (2)	−0.2824 (1)	71 (1)	83 (1)	64 (1)	−7 (1)	−4 (1)	−22 (1)
C9	−0.2007 (1)	−0.0806 (1)	−0.2508 (1)	66 (1)	78 (1)	51 (1)	−14 (1)	−5 (1)	−14 (1)
C10	−0.3524 (2)	−0.0458 (1)	−0.2583 (1)	73 (1)	69 (1)	55 (1)	−16 (1)	−4 (1)	−9 (1)
C11	−0.3843 (2)	−0.2896 (2)	−0.4602 (2)	110 (2)	86 (2)	79 (1)	−36 (1)	−13 (1)	−25 (1)
C12	−0.5445 (2)	−0.2217 (3)	−0.4793 (2)	118 (2)	165 (3)	123 (2)	−52 (2)	−30 (2)	−50 (2)
C13	−0.3520 (4)	−0.4395 (3)	−0.4197 (3)	258 (5)	108 (2)	166 (3)	−94 (3)	−68 (3)	−5 (2)
C14	−0.3054 (3)	−0.2750 (3)	−0.5750 (2)	180 (3)	187 (3)	73 (1)	−69 (3)	−5 (2)	−45 (2)
C15	−0.4912 (2)	0.2445 (2)	−0.0716 (1)	100 (2)	80 (2)	70 (1)	−12 (1)	0 (1)	−25 (1)
C16	−0.6448 (2)	0.2381 (3)	−0.0589 (2)	103 (2)	149 (3)	127 (2)	−17 (2)	26 (2)	−71 (2)
C17	−0.4943 (3)	0.3837 (2)	−0.1311 (2)	188 (3)	76 (2)	113 (2)	−7 (2)	0 (2)	−19 (1)
C18	−0.4327 (3)	0.2257 (2)	0.0446 (2)	163 (3)	139 (2)	66 (1)	−36 (2)	0 (1)	−35 (1)
C19	−0.0207 (2)	0.0660 (2)	−0.2635 (2)	86 (2)	125 (2)	96 (1)	−46 (2)	2 (1)	−33 (1)
C20	0.0814 (3)	−0.0311 (3)	−0.3403 (3)	124 (2)	183 (3)	137 (2)	−70 (2)	48 (2)	−57 (2)
C21	0.0665 (3)	0.0931 (4)	−0.1756 (3)	128 (3)	210 (4)	150 (3)	−84 (3)	−15 (2)	−56 (3)
C22	−0.0860 (3)	0.1993 (3)	−0.3389 (3)	142 (3)	165 (3)	138 (2)	−70 (2)	20 (2)	7 (2)
C23	0.0115 (2)	−0.3156 (2)	−0.2216 (2)	91 (2)	104 (2)	83 (1)	10 (1)	−18 (1)	−26 (1)
C24	0.0564 (3)	−0.2608 (3)	−0.1238 (2)	162 (3)	150 (3)	116 (2)	17 (2)	−78 (2)	−34 (2)
C25	−0.0362 (3)	−0.4380 (2)	−0.1677 (2)	171 (3)	117 (2)	102 (2)	−8 (2)	−30 (2)	−1 (1)
C26	0.1390 (2)	−0.3734 (3)	−0.3020 (2)	98 (2)	158 (3)	135 (2)	25 (2)	1 (2)	−50 (2)

Atom	x	y	z	B	Atom	x	y	z	B
H1[b]	−0.211 (2)	0.187 (2)	−0.129 (1)	2.0 (3)	H21	−0.337 (4)	0.250 (4)	0.038 (3)	6.4 (7)
H2	−0.550 (2)	0.074 (2)	−0.208 (1)	1.7 (3)	H22	−0.429 (3)	0.129 (3)	0.084 (2)	5.5 (6)
H3	−0.516 (2)	−0.085 (2)	−0.328 (2)	2.0 (3)	H23	0.030 (3)	−0.063 (3)	−0.397 (2)	4.7 (6)
H4	−0.126 (2)	−0.361 (2)	−0.379 (2)	2.2 (3)	H24	0.148 (4)	−0.126 (4)	−0.292 (3)	6.5 (7)
H5	−0.581 (3)	−0.255 (3)	−0.397 (2)	4.4 (6)	H25	0.131 (3)	0.032 (3)	−0.388 (2)	5.8 (7)
H6	−0.578 (3)	−0.272 (3)	−0.536 (2)	4.1 (5)	H26	0.006 (3)	0.171 (3)	−0.127 (2)	5.5 (6)
H7	−0.570 (3)	−0.116 (3)	−0.505 (2)	4.8 (6)	H27	0.143 (3)	0.129 (3)	−0.214 (2)	5.6 (6)
H8	−0.418 (2)	−0.430 (2)	−0.349 (2)	2.7 (4)	H28	0.097 (3)	0.015 (3)	−0.123 (2)	5.3 (6)
H9	−0.238 (3)	−0.489 (3)	−0.412 (2)	5.4 (6)	H29	−0.148 (4)	0.167 (3)	−0.402 (3)	6.6 (7)
H10	−0.381 (4)	−0.485 (4)	−0.476 (3)	7.0 (8)	H30	−0.018 (4)	0.237 (3)	−0.379 (3)	6.4 (7)
H11	−0.336 (3)	−0.324 (3)	−0.629 (2)	5.4 (6)	H31	−0.146 (4)	0.276 (4)	−0.286 (3)	6.6 (7)
H12	−0.319 (3)	−0.160 (3)	−0.600 (2)	4.6 (6)	H32	−0.028 (4)	−0.234 (4)	−0.066 (3)	7.1 (8)
H13	−0.198 (4)	−0.336 (4)	−0.561 (3)	7.2 (8)	H33	0.129 (3)	−0.342 (3)	−0.076 (2)	4.7 (6)
H14	−0.699 (2)	0.256 (2)	−0.137 (2)	3.3 (4)	H34	0.094 (4)	−0.169 (4)	−0.151 (3)	6.6 (8)
H15	−0.650 (3)	0.143 (3)	−0.018 (2)	4.5 (6)	H35	−0.128 (4)	−0.404 (4)	−0.113 (3)	7.5 (8)
H16	−0.706 (3)	0.316 (3)	−0.012 (2)	5.6 (6)	H36	−0.053 (3)	−0.490 (3)	−0.228 (2)	5.1 (6)
H17	−0.393 (3)	0.391 (3)	−0.127 (2)	4.7 (6)	H37	0.048 (3)	−0.511 (3)	−0.113 (3)	5.9 (7)
H18	−0.523 (3)	0.393 (3)	−0.213 (3)	5.9 (7)	H38	0.111 (3)	−0.415 (3)	−0.368 (2)	5.2 (6)
H19	−0.553 (3)	0.458 (3)	−0.090 (2)	5.0 (6)	H39	0.177 (4)	−0.294 (4)	−0.343 (3)	8.5 (9)
H20	−0.494 (3)	0.297 (3)	0.092 (2)	5.2 (6)	H40	0.219 (4)	−0.449 (4)	−0.262 (3)	6.8 (8)

[a] The anisotropic temperature factor expression used for the C atoms is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. For the H atoms a temperature factor of the form $\exp(-B \sin^2 \theta/\lambda^2)$ was used. [b] H_1 is bonded to C_2; H_2 to C_4; H_3 to C_5; H_4 to C_7; H_5, H_6, and H_7 to C_{12}; H_8, H_9, and H_{10} to C_{13}; etc.

Consideration of molecular models led to the conclusion that there are three conformational arrangements of the *tert*-butyl groups which seemed a priori to be reasonable and these have symmetries C_{2v}, C_s, and C_2. Actually, there are two C_{2v} conformations possible. In one, a methyl group of each *tert*-butyl lies in the naphthalene plane and points toward the other methyl. This conformation was dismissed as clearly being of high energy, and only the other C_{2v} conformation, in which the coplanar methyls point away from each other, was considered. The C_{2v} structure studied seems to be an energy maximum, rather than a minimum. In any case, the C_{2v} and C_s symmetries were placed upon the respective conformations as constraints. Only the C_2 point group would allow a nonplanar naphthalene, whereas the first two point groups require a planar aromatic framework. The results of the calculations are summarized in Table IV. Note that the calculations were carried out on di-*tert*-butylnaphthalene, while the x-ray work was on the tetra-*tert*-butyl derivative.

Results and Discussion

The bond distances and bond angles and their standard deviations, determined for the carbon atoms by crystallography, are given in Table III. The esd's range from 0.002 to 0.004 Å for the C–C bonds and 0.01 to 0.04 Å for the C–H bonds. The structure is illustrated by two stereoscopic ORTEP plots (Figure 1).[12]

Comparison of the distances and angles in the two crystallographically independent halves of the molecule (Table III, Figure 1) shows that the molecule does in fact contain a two-fold axis, within experimental error, parallel to the C_9–C_{10} bond. This result was confidently predicted by the mechanics calculations as shown by the large energy differences from the other two structures considered in Table IV. For convenience,

Table III. Bond Distances and Bond Angles Involving the Carbon Atoms

Atoms		Distance, Å	Atoms			Angle, deg	Atoms			Angle, deg
C1	C2	1.377 (2)	C6	C11	C13	110.7 (2)	C2	C1	C9	117.4 (1)
C1	C9	1.454 (2)	C6	C11	C14	107.3 (2)	C2	C1	C19	114.3 (2)
C1	C19	1.558 (3)	C12	C11	C13	111.0 (2)	C9	C1	C19	125.6 (1)
C2	C3	1.417 (2)	C12	C11	C14	106.6 (2)	C1	C2	C3	124.5 (2)
C3	C4	1.362 (2)	C13	C11	C14	108.7 (2)	C2	C3	C4	116.2 (1)
C3	C15	1.526 (2)	C3	C15	C16	111.5 (2)	C2	C3	C15	119.6 (1)
C4	C10	1.415 (2)	C3	C15	C17	108.9 (2)	C4	C3	C15	123.8 (1)
C5	C6	1.361 (2)	C3	C15	C18	109.6 (1)	C3	C4	C10	121.8 (1)
C5	C10	1.417 (2)	C16	C15	C17	108.6 (2)	C6	C5	C10	121.7 (1)
C6	C7	1.420 (2)	C16	C15	C18	108.3 (2)	C5	C6	C7	115.8 (1)
C6	C11	1.521 (2)	C17	C15	C18	109.9 (2)	C5	C6	C11	124.2 (1)
C7	C8	1.376 (2)	C1	C19	C20	115.5 (2)	C7	C6	C11	119.6 (1)
C8	C9	1.443 (2)	C1	C19	C21	113.3 (2)	C6	C7	C8	124.6 (2)
C8	C23	1.557 (2)	C1	C19	C22	104.5 (2)	C7	C8	C9	117.6 (1)
C9	C10	1.433 (2)	C20	C19	C21	108.7 (2)	C7	C8	C23	114.5 (1)
C11	C12	1.536 (3)	C20	C19	C22	105.3 (2)	C9	C8	C23	125.8 (1)
C11	C13	1.514 (3)	C21	C19	C22	108.9 (2)	C1	C9	C8	129.9 (1)
C11	C14	1.558 (3)	C8	C23	C24	113.6 (2)	C1	C9	C10	115.1 (1)
C15	C16	1.537 (3)	C8	C23	C25	106.6 (2)	C8	C9	C10	115.0 (1)
C15	C17	1.528 (3)	C8	C23	C26	112.9 (2)	C4	C10	C5	118.9 (1)
C15	C18	1.528 (3)	C24	C23	C25	104.7 (2)	C4	C10	C9	120.5 (1)
C19	C20	1.536 (4)	C24	C23	C26	111.9 (2)	C5	C10	C9	120.6 (1)
C19	C21	1.528 (4)	C25	C23	C26	106.5 (2)	C6	C11	C12	112.3 (2)
C19	C22	1.539 (4)								
C23	C24	1.534 (3)								
C23	C25	1.550 (3)								
C23	C26	1.544 (3)								

the intramolecular distances from the crystal structure have been averaged in the two halves of the molecule for comparison with the calculated values.

The agreement between calculation and experiment is good (Table IV). Crystal packing forces are expected to distort the molecule slightly, so exact agreement with the calculated (gas phase) values is not expected. The nonplanarity of the naphthalene is quite marked, with each benzene ring distorted into a flattened half-chair shape. Owing to this distortion, there is no aromatic plane which can serve as a standard of comparison. For the sake of discussion, we have defined a *mean plane* using the aromatic 2, 4, 5, 7, 9, and 10 carbons. The resultant computation shows C_9 and C_{10} in the plane and C_2 and C_7 very nearly in the plane (Table V). The peri carbons 1 and 8 are 0.29 Å above and below the mean plane of the molecule by calculations and by experiment. (Figure 2.) The *tert*-butyl carbons bonded to the peri positions are twisted further from the mean plane, placing them 1.22 Å above and below the plane, by experiment, or 1.19 Å by calculation. The difference is 15 times σ and is significant (Figure 2). Thus, we see that the force field places a slightly greater restriction on the out-of-plane deformation than is actually observed. The opposite peri carbons 4 and 5 are 0.13 Å experimentally (0.14 Å calculated) below and above the mean plane, a less serious distortion.

A search for methyl–methyl repulsion reveals only three serious interactions with distances significantly less than 4 Å, the sum of the contact radii for two methyl groups.[13] In locating the specific hydrogen atom repulsions which are the culprits in these repulsions, assuming a fixed rotamer of the methyls, one finds only three H–H distances of 2 Å or less (Figure 3). This observation reinforces our understanding of strain minimization where it has been clear that enormous angular and torsional distortion will occur before much interpenetration of van der Waals radii becomes energetically acceptable. Nevertheless, a small part of the strain energy is taken up in repulsion; otherwise the angular distortions would be even greater.

An interesting feature of the nonplanarity of the peri carbons is the confirmation of an interpretation of the electron spin

Table IV. Bond Distances and Angles of Tetra-*tert*-butylnaphthalene

	Calcd			Exptl
	C_s	C_{2v}	C_2	
Bonds, Å				
1-9	1.470	1.490	1.450	1.454
1-2	1.386	1.391	1.384	1.377
1-19	1.537	1.577	1.553	1.558
4-10	1.425	1.427	1.427	1.415
9-10	1.431	1.442	1.417	1.433
Nonbonded distances, Å				
1-8	2.68	2.74	2.60	2.623
4-5	2.39	2.34	2.45	2.439
19-23	3.53	3.96	3.80	3.861
20-24	3.01	3.21	3.53	3.367
20-26	3.01	3.57	3.42	3.407
21-24	3.98	3.59	3.54	3.697
Angles, deg				
9-1-19	130.5	136.2	126.5	125.6
9-1-2	120.0	118.0	117.8	117.4
19-1-2	109.5	105.8	113.3	114.3
1-9-8	131.3	133.3	127.2	129.9
1-9-10	114.3	113.3	116.4	115.1
4-10-5	113.8	110.4	118.5	118.5
Dipole moment, D	0.58	0.55	0.48	
Heat of formation, kcal/mol			23.88	
Strain (rel to 1,5-di-*tert*-butylnaphthalene)			21.54	
Relative energies	18.47	25.30	0.00	

resonance spectra of these naphthalenes.[14] In order to fit the unusual hyperfine splittings in the ESR spectra in this series with MO calculations, the p orbitals on peri carbons 1 and 8 were required to be 20–25° out of alignment with the orbitals on carbons 2 and 7. In this conformation there could be leakage
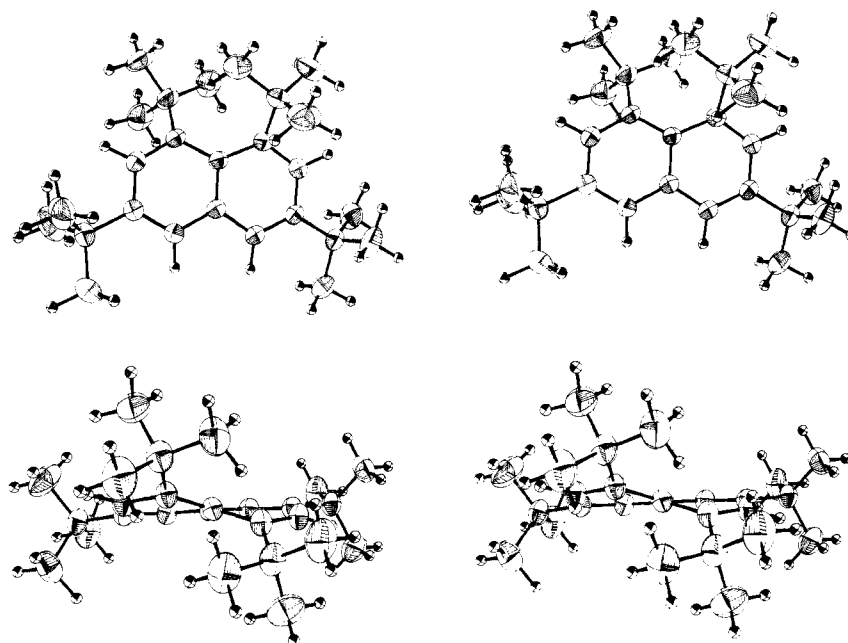
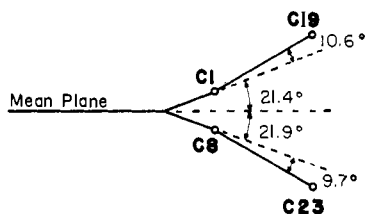Figure 1. Stereoscopic ORTEPs of two views of the x-ray structure of naphthalene 3.

Figure 2. Projection of the distortion of atoms 1, 8, 19 and 23 from the mean plane described by atoms 2, 4, 5, 7, 9, and 10 (experimental value).
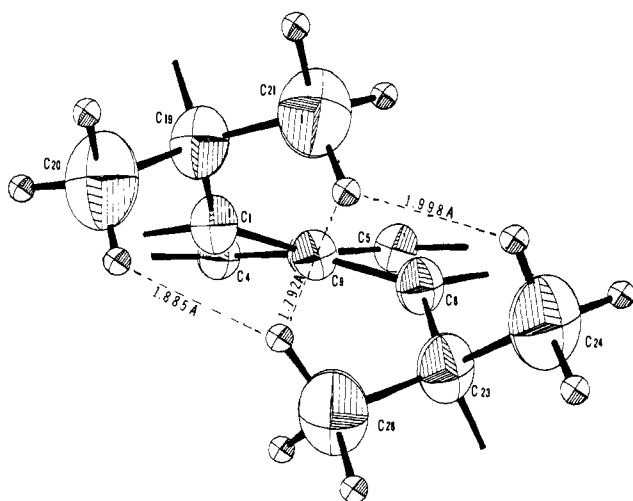
Table V. Deviations from Mean Plane (Defined by Carbons 2, 4, 5, 7, 9, and 10)

Carbon	Calcd C_2 Å	Exptl Å
1	0.29	0.29
2	0.07	0.07
3	−0.21	−0.21
4	−0.14	−0.13
19	1.19	1.22

Figure 3. Observed close contacts among hydrogen on peri tert-butyl groups (experimental value).

of spin density toward the hydrogen nuclei with an effect opposite to that caused by the normal spin-polarization mechanism in planar aromatic species where the σ framework is orthogonal to the π network.

It has been concluded from the observation of diastereotopic hydrogens in the NMR spectrum of benzylnaphthalene 4 that the aromatic framework was nonplanar and chiral.[14] Further, from coalescence studies, it was determined that the free en-

ergy of the barrier to racemization was greater than 20 kcal/mol. The tert-butyls and the peri carbons must pass through the mean plane of the molecule for racemization to occur, and our model of the transition state has this all happening simultaneously. However, it should be pointed out that racemization could occur with one ring passing through the plane, followed by the other. In this pathway, there are no achiral states. We consider the former, simultaneous, model of the transition state as reasonable. This possibility corresponds to the geometries calculated for the C_{2v} and C_s point groups. The calculated energy difference between the C_2 conformation and the lower of the C_{2v} or C_s may then be considered to be approximately the difference between the ground state and transition state for the racemization process. Thus, a barrier enthalpy of 18.5 (C_s) kcal/mol is calculated. Since the transition state is more congested than the ground state, the activation entropy is likely to be negative. The calculated enthalpic value for the barrier is therefore considered to be in reasonable agreement with that of the NMR experiment which is a determination of the free-energy barrier.

In conclusion, the peri-tert-butylnaphthalene system is seriously distorted from planarity. While aromatic rings tend to be planar, they do undergo out-of-plane bending when sufficient force is applied.[16] Furthermore, the deformation can be reasonably well predicted using the methods of molecular mechanics.

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Novel Aromatic Systems. 8.[1] Cyclooctatetraene Dications

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Abstract: Suitably substituted cyclooctatetraenes are oxidized by antimony pentafluoride in sulfuryl chloride fluoride solution to the corresponding C_8 6 π-electron Hückeloid cyclooctatetraene dications. The structures of the 1,4-dimethyl-, 1,3,5,7-tetramethyl-, 1,3,5,7-tetraphenyl-, and *sym*-dibenzocyclooctatetraene dications are discussed in terms of their ^{1}H and ^{13}C NMR spectra.

For over 150 years chemists have been intrigued by that group of unsaturated organic molecules which they termed "aromatic".[3] The concept and theory of aromaticity was first placed on a sound physical foundation during 1931–1937 with Hückel's[3-6] development of the basic pattern of molecular orbital theory of unsaturated and aromatic compounds. Hückel's rule and subsequent more highly refined theoretical treatments of aromaticity[7] have stimulated continued efforts to prepare molecules designed to provide the experimental tests for their predictions. This experimental work has led to the discovery of a substantial number of intriguing new "aromatic" molecules, highlighted by the cyclopropenium ion (**1**),[8] the cyclopentadienyl anion (**2**),[9] the tropylium ion (**3**),[10] the cyclononatetraenyl anion (**4**),[11] the cyclooctatetraene dianion (**5**),[12] the annulenes,[13] the bridged annulenes,[13] and the
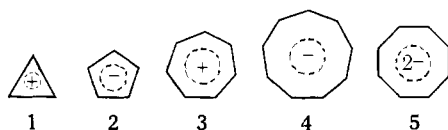
trans-15,16-dihydropyrenes.[14] Not withstanding their predicted aromatic stabilization,[3,5,7,15] several fundamental systems have remained elusive of preparation and experimental study. Perhaps the most notable Hückeloid absentee is the C_8 6 π-electron cyclooctatetraene dication (**6**). Despite repeated attempts,[16,17] neither **6** nor any of its substituted derivatives have yet yielded to synthesis.

Cyclooctatetraene (**7**) is a nonplanar 8 π-electron system[18] which occupies an extremely interesting pivotal position for the preparation of the cyclooctatetraene dication (**6**) since a
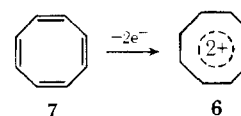
two-electron oxidation offers the possibility of its conversion into the 6 π-electron dication **6**.

In a communication[1b] we reported the first successful preparation of a cyclooctatetraene dication, namely, the 1,3,5,7-tetramethyl derivative, by the 2 π-electron oxidation of the respective cyclooctatetraene[19] with SbF_5 in SO_2ClF solution at low temperature. We now wish to report our complete studies in this area which includes the preparation and study of a series of cyclooctatetraene dications.

Results and Discussion

A. The 1,4-Dimethylcyclooctatetraene Dication. Antimony pentafluoride in sulfuryl chloride fluoride (SbF_5–SO_2ClF) solution has recently been shown to be an effective two-electron oxidizing agent, particularly for the oxidation of aromatic hydrocarbons to their respective dications.[20] Treatment of 1,4-dimethylcyclooctatetraene (**8**)[21] with SbF_5–SO_2ClF at −78 °C results in the formation of the corresponding 1,4-dimethylcyclooctatetraene dication (**9**). The ^{1}H NMR spec-