Structural Analysis of Internally Crowded Naphthalene Derivatives. *peri*-Diphenylacenaphthene[1a]

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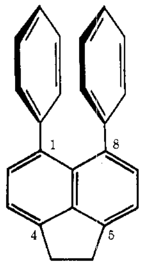
The sterically crowded *peri*-diphenylacenaphthene (1) has been synthesized by an aryl–aryl coupling reaction, and its conformation in the crystal determined by x-ray diffraction. The strain induced by nonbonded interactions between the phenyl groups greatly affects the geometry of the molecule as a whole. The phenyl rings are face to face, making an angle of 57° to the naphthalene plane, and are splayed apart. The phenyl to naphthalene bonds are nearly identical in length with the interannular bonds of biphenyl and *p*-terphenyl, in which the aromatic rings are coplanar. A comparison is made of the structures of 1,8-diphenylnaphthalene, *peri*-diphenylacenaphthene, and 1,4,5,8-tetraphenylnaphthalene, which constitute a homologous series of *peri*-phenylnaphthalenes differing only in the arrangement of groups at one end of the molecule. Substantial deformations of angles and bond lengths in the naphthalene framework of these compounds are analyzed in terms of force vectors acting throughout the bonding skeleton. This analysis helps to explain the surprising ease of rotation about the interannular C–C bonds in these compounds. The ^{1}H NMR spectrum of 1 indicates that the preferred conformation in solution is analogous to that in the crystal.

There has been considerable recent interest in the properties and structures of 1,8-disubstituted naphthalene derivatives.[2] Such compounds are expected to exist in a state of high steric stress, owing to overcrowding of the substituents which are held in close proximity by approximately parallel bonds to the relatively rigid naphthalene framework. Recent NMR[3] and x-ray diffraction[4] studies have shown that relief of the steric stress is accomplished by splaying of the bonds to the peri substituents as well as by surprisingly large in-plane and out-of-plane deformations of the naphthalene nucleus itself. In another series of NMR experiments,[5] it has been shown that the barriers to rotation about the exocyclic bonds at the 1 and 8 positions are surprisingly small, even for bulky substituents. Developing a further understanding of the geometry of this class of compounds is therefore both important and timely.

We report here the synthesis, ^{1}H NMR spectrum, and crystal structure of *peri*-diphenylacenaphthene (1). In this compound, the overcrowding of the phenyl groups at the 1 and 8 positions is accompanied by a pinching together at the 4 and 5 positions, due to the bridging ethylene group. We compare its molecular structure with those previously determined[6,7] for 1,8-diphenylnaphthalene (2), where there are no additional interactions at the 4 and 5 positions, and for 1,4,5,8-tetraphenylnaphthalene (3), which shows overcrowding at both the 1,8 and 4,5 positions. We also analyze the various distorting forces that arise from these stresses, and their effects on the geometry of the naphthalene nucleus. Finally, we shall see that the ground-state geometry of the 1,8-diphenylnaphthalene system is such as to explain the relatively low energy barrier to rotation about the C(naphthyl)–C(phenyl) bonds.[5a]



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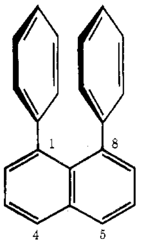

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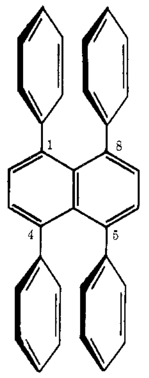

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Experimental Section

peri-Diphenylacenaphthene (1) was synthesized in five steps from acenaphthene. The key step was a nickel-catalyzed coupling between *peri*-diiodoacenaphthene and phenylmagnesium iodide which proceeded in 78% yield to give 1.[8] *peri*-Diiodoacenaphthene was prepared in four steps from acenaphthene essentially in accord with procedures described in the literature;[9,10] an overall yield of 1% was obtained as colorless needles of mp 157–159 °C (lit.[10] 159–160 °C); NMR ($CDCl_3$) δ 3.30 (s, 4 H), 7.59 (AB q, 4 H). Phenylmagnesium iodide was generated from 0.49 g (20 mmol) of magnesium and 4.12 g (20 mmol) of iodobenzene in 20 ml of ether containing 5 ml of benzene. Half of the Grignard solution was added during a 2-h period to a stirred mixture of 0.41 g (1 mmol) of 5,6-diiodoacenaphthene and 0.005 g (0.027 mmol) of nickel acetylacetonate dissolved in 16 ml of benzene and 8 ml of ether held at −14 to −10 °C. The reaction mixture was stirred for an additional 2.5 h at this temperature, allowed to warm to room temperature overnight, and then hydrolyzed with saturated aqueous ammonium chloride solution. The crude mixture was chromatographed on 80 g of silica with hexane as the eluent and gave 0.240 g (78% based on diiodoacenaphthene) of 1. Recrystallization from hexane afforded clear prisms of mp 156–157 °C; mass spectrum, parent *m/e* peak 306.1410 (calcd for $C_{24}H_{18}$, 306.1408); NMR ($CDCl_3$) δ 3.43 (s, 4 H), 6.87 (s, 10 H), 7.30 (s, 4 H). The ultraviolet spectrum kindly determined by Anne C. Cain showed λ_{max} 311 nm (ϵ 15 200) with a shoulder at 330 nm (ϵ 10 200) at 5×10^{-5} M in hexane solution.

Crystal Structure Analysis. The crystals of 1 used for x-ray studies were obtained by slow evaporation of a hexane solution. They were pale-yellow prisms, elongated along *b*. Preliminary Weissenberg photographs suggested the triclinic space group $P\bar{1}$, which was confirmed by the structure analysis. Lattice constants were derived from a least-squares fit to 15 2θ values ranging between 105 and 120°, measured on a quarter-circle diffractometer using Cu Kα radiation. The density was measured by flotation in aqueous solutions of $ZnBr_2$. The crystal data are given in Table I.

A crystal approximately 0.43 × 0.23 × 0.10 mm in size was mounted along the long dimension (*b* axis) and used for data collection. Intensities were measured using a Datex-automated General Electric three-circle diffractometer equipped with a copper-target x-ray tube, Ni filter, scintillation counter, and pulse-height analyzer. Data were collected up to a 2θ value of 150° using a θ–2θ scan mode at a scan rate of 1° per minute; the scan width varied from 2.0° at $2\theta = 5°$ to 3.0° at $2\theta = 150°$. The takeoff angle was 3.0°. A 30-s background count was recorded at each scan extremum. A check reflection $(1,\bar{1},1)$ was recorded every 30 reflections and two other check reflections $(2,\bar{1},\bar{1})$, $(3,1,\bar{1}\bar{0})$ were recorded every 60 reflections. These reflections all showed slow decay, reaching 3% in *F* at the end of the data collection. The recorded intensities were corrected for this decay, and for Lorentz and polarization effects; no absorption corrections were applied ($\mu = 5.4$ cm^{-1}). Observational variances $\sigma^2(I)$ were assigned on the basis of counting statistics plus an additional term $(0.02S)^2$, where *S* is the scan count. Two equivalent data sets were collected; they showed excellent agreement, and the averaged set was used for final refine-

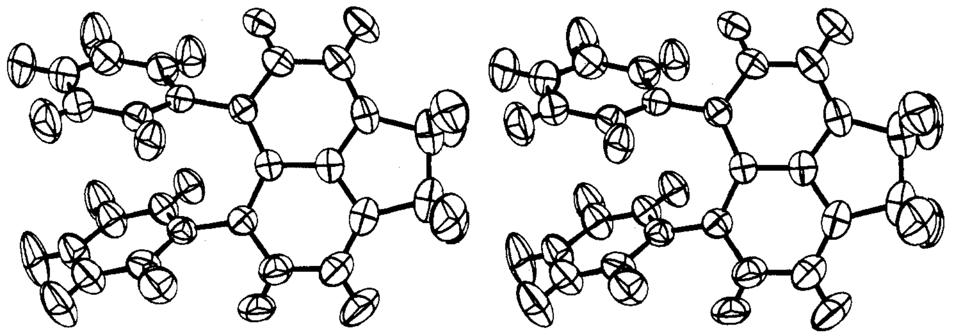

Figure 1.

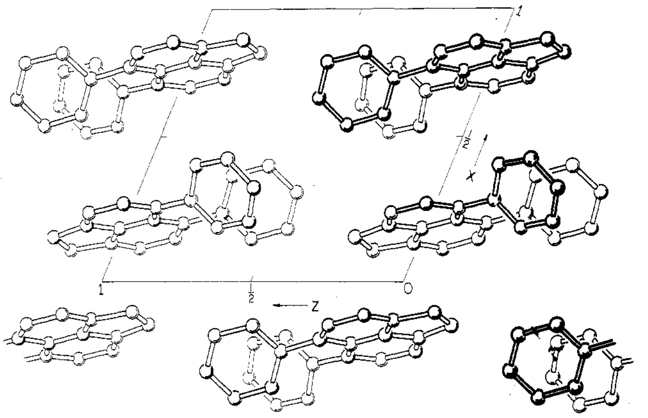

Figure 2.

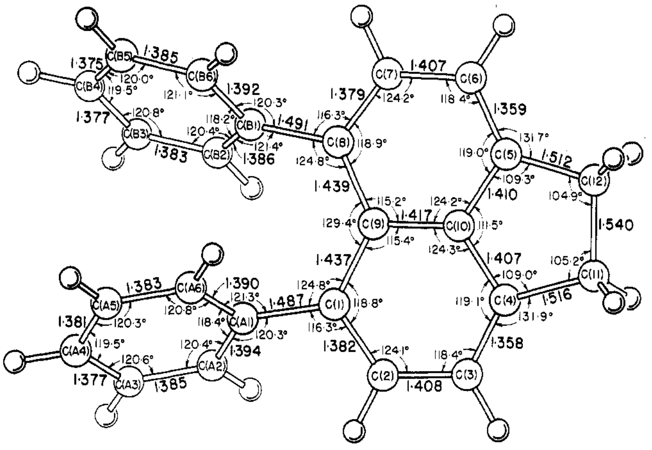

Figure 3.

ment. The total number of independent reflections was 3404, of which 154 had averaged intensities less than zero.

Approximate coordinates for the ten atoms of the naphthalene ring were obtained from a three-dimensional Patterson map. Structure factors based on these ten atoms yielded an R index, $\Sigma||F_c| - |F_o||/\Sigma|F_o|$, of 0.63 and a subsequent Fourier map revealed the positions of the remaining carbon atoms. Initial coordinates for the 18 hydrogen atoms were calculated assuming C–H distances of 1.0 Å and idealized trigonal or tetrahedral bonding around the carbon atoms. Refinement involved least-squares minimization of the quantity $\Sigma w(F_o^2 - F_c^2)^2$ with weights, w, equal to $\sigma^{-2}(F_o^2)$. In the final cycles, in which 380 parameters were adjusted, three matrices were collected: the coordinates of all 42 atoms were in one matrix; the scale factor, a secondary extinction coefficient,[12] and the anisotropic temperature parameters of the carbon atoms were in a second matrix; and the anisotropic temperature parameters of the hydrogen atoms were in a third. After four such cycles, no parameter shifted by more than 0.6 σ. The final goodness-of-fit $[\Sigma w(F_o^2 - F_c^2)^2/(N - P)]^{1/2}$ for N = 3404 reflections and P = 380 parameters was 2.56; the R index was 0.040 for the 3250 reflections with net intensities greater than zero. A final difference Fourier map showed no peak greater than 0.18 eÅ^{-3}.

Table I. Crystal Data

5,6-Diphenylacenaphthene	$C_{24}H_{18}$
Triclinic	Mol wt 306.4
Space group $P\bar{1}$	$Z = 2$
a = 10.493 (3) Å	$F(0,0,0) = 324$
b = 7.861 (3)	$\rho_{\text{meas}} = 1.22$ g cm^{-3}
c = 11.567 (4)	$\rho_{\text{calcd}} = 1.23$ g cm^{-3}
α = 71.25 (1)	μ = 5.4 cm^{-1} (for Cu Kα radiation)
β = 113.43 (1)	λ (Cu Kα = 1.5418 Å
γ = 94.90 (1)	R = 0.040 (3250 data points)
V = 828.0 Å^3	

Results and Discussion

The final coordinates and anisotropic temperature parameters are given in Table II.[13] A stereoscopic view of the molecule is shown in Figure 1, and a packing drawing of the structure is shown in Figure 2. Bond distances and angles between the carbon atoms are shown in Figure 3; the esd's in these values are about 0.002 Å and 0.1°. Distances and angles involving the hydrogen atoms are listed in Table III. The bond distances and angles have not been corrected for effects of thermal libration because we have been unable to satisfactorily explain the anisotropic thermal parameters (Table II) in terms of any reasonable pattern of rigid-body motions. In any event, the thermal motion of the important acenaphthene grouping is quite small, and corrections to the bond distances and angles in this portion of the molecule should be no greater than the standard deviations.

Deviations of the carbon atoms from the least-squares plane[14] through atoms C(1)–C(10) are included in Figure 4. The bridging ethano carbon atoms C(11) and C(12) lie close to this plane (deviations: +0.034 and −0.025 Å), and the torsion angle about the C(11)–C(12) bond is only 2.3°. The eclipsing of the protons on these adjacent carbon atoms results in noticeable bond-angle deformation: the four angles of the type C(11)–C(12)–H (av 113°) are consistently larger than the four of the type C(5)–C(12)–H (av 110°). This deformation increases the H···H distances to 2.32 and 2.33 Å, slightly shorter than the normal van der Waals distance of 2.4 Å.[15] The angles C(4)–C(11)–C(12) (105.2°) and C(5)–C(12)–C(11) (104.9°) are smaller than the C–C–C angles in linear alkanes, which average about 112°.[16] This angle reduction is *not* accompanied by an appreciable opening of the H–C–H angles; the values of 106 and 105° are comparable with the average value of about 107° for linear alkyl groups.[17] Naphtho[*b*]cyclobutene (4) shows similar behavior.[18] The C–C–C angles at the methylene groups of 4 are constrained to an even

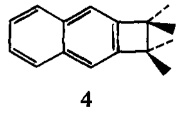

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Table II. Final Coordinates and Anisotropic Temperature Parameters (× 10^4 for C; × 10^3 for H) for *peri*-Diphenylacenaphthene[a]

	X	*Y*	*Z*	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
C1	2740 (1)	−1228 (1)	−811 (1)	92 (1)	180 (2)	83 (1)	−5 (2)	60 (2)	−64 (2)
C2	2866 (1)	−2653 (2)	311 (1)	121 (1)	192 (2)	90 (1)	17 (3)	63 (2)	−36 (3)
C3	2540 (1)	−2523 (2)	1350 (1)	127 (1)	259 (3)	81 (1)	−3 (3)	73 (2)	−16 (3)
C4	2078 (1)	−901 (2)	1254 (1)	101 (1)	283 (3)	79 (1)	−31 (3)	70 (2)	−95 (3)
C5	1426 (1)	2141 (2)	178 (1)	110 (1)	265 (3)	122 (1)	−61 (3)	110 (2)	−193 (3)
C6	1220 (1)	3692 (2)	−845 (1)	154 (2)	214 (3)	169 (2)	−38 (3)	166 (3)	−184 (3)
C7	1594 (1)	3692 (2)	−1886 (1)	148 (2)	171 (2)	149 (2)	−32 (3)	154 (3)	−99 (3)
C8	2132 (1)	2203 (1)	−1953 (1)	102 (1)	169 (2)	106 (1)	−39 (2)	97 (2)	−87 (2)
C9	2297 (1)	516 (1)	−920 (1)	86 (1)	184 (2)	84 (1)	−31 (2)	68 (2)	−87 (2)
C10	1957 (1)	584 (1)	134 (1)	89 (1)	225 (2)	91 (1)	−44 (3)	70 (2)	−117 (2)
C11	1627 (1)	−305 (2)	2162 (1)	131 (2)	415 (4)	94 (1)	−18 (4)	98 (2)	−147 (4)
C12	1158 (1)	1694 (2)	1432 (1)	138 (2)	361 (4)	133 (2)	−64 (4)	130 (3)	−249 (4)
CA1	3009 (1)	−1660 (1)	−1858 (1)	118 (1)	155 (2)	94 (1)	6 (2)	92 (2)	−57 (2)
CA2	4278 (1)	−2477 (2)	−1560 (1)	143 (2)	250 (3)	115 (1)	93 (3)	102 (2)	−51 (3)
CA3	4510 (2)	−2946 (2)	−2519 (2)	206 (2)	297 (3)	159 (2)	156 (4)	206 (3)	−60 (4)
CA4	3492 (2)	−2621 (2)	−3776 (1)	236 (2)	263 (3)	138 (2)	32 (4)	219 (3)	−114 (4)
CA5	2229 (2)	−1817 (2)	−4082 (1)	184 (2)	226 (3)	103 (1)	−62 (4)	128 (3)	−108 (3)
CA6	1985 (1)	−1355 (1)	−3128 (1)	125 (1)	173 (2)	96 (1)	−27 (3)	89 (2)	−70 (2)
CB1	2538 (1)	2492 (1)	−3097 (1)	110 (1)	151 (2)	97 (1)	−36 (2)	92 (2)	−59 (2)
CB2	3887 (1)	2118 (2)	−2907 (1)	104 (1)	229 (2)	97 (1)	−37 (3)	82 (2)	−67 (3)
CB3	4251 (1)	2453 (2)	−3983 (1)	122 (2)	321 (3)	117 (1)	−23 (3)	127 (2)	−77 (3)
CB4	3285 (2)	3173 (2)	−5259 (1)	167 (2)	335 (4)	104 (1)	1 (4)	136 (3)	−56 (3)
CB5	1947 (2)	3573 (2)	−5463 (1)	160 (2)	286 (3)	93 (1)	34 (4)	79 (3)	−21 (3)
CB6	1576 (1)	3241 (2)	−4391 (1)	119 (1)	201 (2)	1 (1)	20 (3)	83 (2)	−46 (3)
H11	242 (1)	−49 (2)	305 (1)	14 (2)	63 (5)	10 (2)	5 (5)	3 (3)	−28 (5)
H11′	87 (1)	−106 (2)	234 (1)	19 (2)	33 (4)	16 (2)	−7 (4)	19 (3)	−12 (4)
H12	13 (1)	196 (2)	121 (1)	13 (2)	44 (4)	21 (2)	5 (4)	22 (3)	−17 (5)
H12′	169 (1)	251 (2)	196 (1)	25 (3)	40 (4)	16 (2)	−27 (5)	19 (4)	−34 (5)
H2	318 (1)	−386 (1)	38 (1)	19 (2)	18 (3)	11 (2)	6 (4)	14 (3)	0 (3)
H3	269 (1)	−364 (2)	215 (1)	21 (2)	27 (3)	10 (2)	1 (4)	13 (3)	4 (3)
H6	82 (1)	484 (2)	−86 (1)	24 (2)	23 (3)	26 (2)	−6 (4)	28 (4)	−30 (4)
H7	150 (1)	487 (2)	−261 (1)	26 (2)	13 (2)	19 (2)	2 (4)	28 (4)	−3 (4)
HA2	502 (1)	−273 (2)	−64 (1)	16 (2)	43 (4)	11 (2)	16 (4)	7 (3)	−12 (4)
HA3	546 (1)	−351 (2)	−230 (1)	22 (3)	66 (5)	13 (2)	42 (6)	13 (4)	−14 (5)
HA4	367 (2)	−297 (2)	−448 (1)	35 (3)	41 (4)	16 (2)	10 (5)	34 (4)	−19 (5)
HA5	148 (1)	−153 (2)	−499 (1)	20 (2)	37 (4)	8 (1)	−5 (4)	5 (3)	−13 (4)
HA6	106 (1)	−79 (2)	−335 (1)	11 (2)	29 (3)	11 (1)	−2 (3)	5 (2)	−18 (3)
HB2	459 (1)	161 (2)	−198 (1)	11 (2)	32 (3)	9 (1)	3 (4)	6 (2)	−5 (3)
HB3	523 (1)	212 (2)	−383 (1)	13 (2)	54 (5)	11 (2)	10 (5)	12 (3)	−8 (4)
HB4	356 (1)	341 (2)	−606 (1)	23 (2)	72 (6)	10 (2)	−2 (6)	22 (3)	−14 (5)
HB5	124 (1)	415 (2)	−640 (1)	19 (2)	50 (4)	8 (2)	13 (5)	5 (3)	0 (4)
HB6	63 (1)	355 (2)	−452 (1)	13 (2)	30 (3)	14 (2)	8 (4)	12 (3)	−6 (4)

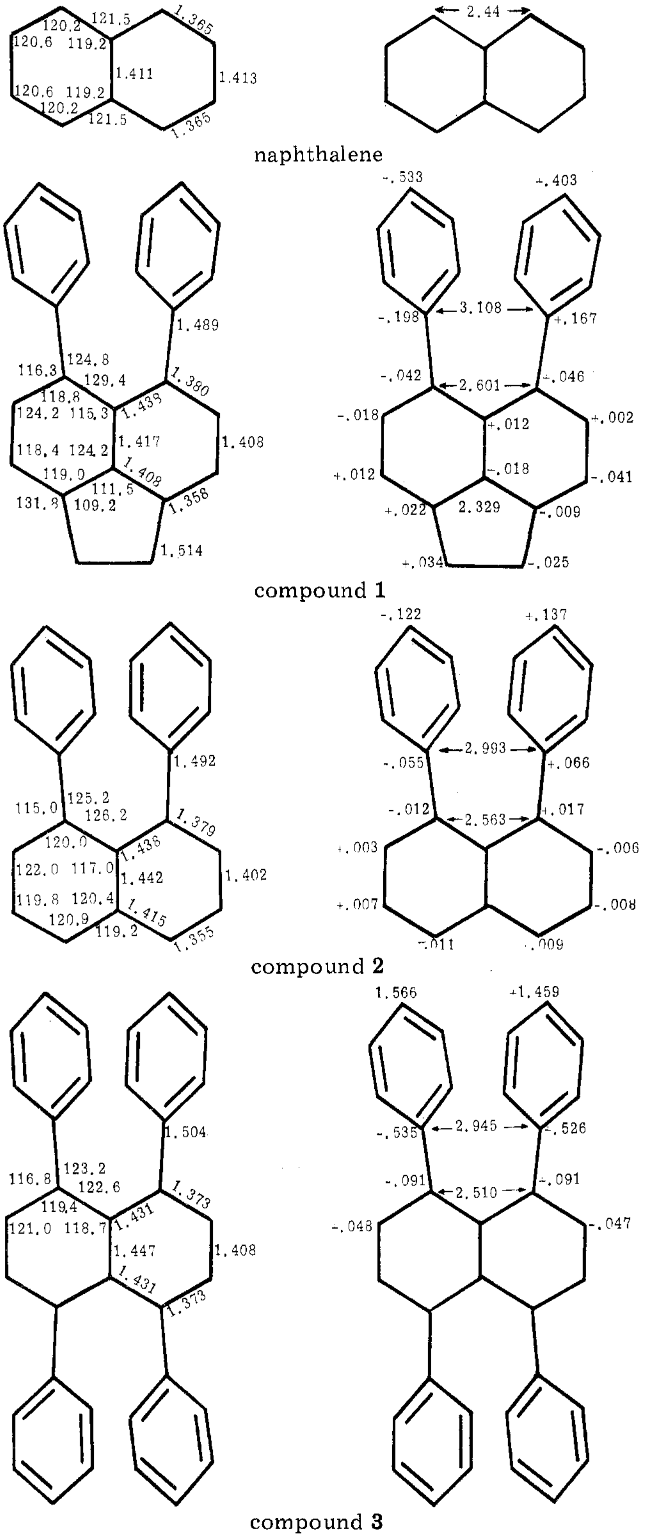
[a] The temperature parameters are of the form $\exp -2\pi^2(U_{11}h^2a^{*2} \ldots + 2U_{23}klb^*c^*)$.

smaller value (87°), but the H–C–H angles remain at 107°. This lack of change seems surprising. The pulling together of the two pairs of C–C bonding electrons should reduce their repulsion with the two C–H bonding pairs, so that these C–H pairs can move farther apart. Further accurate data on H–C–H angles in small-ring compounds are scarce; this point merits further experimental investigation.

The two phenyl rings are positioned face to face, and both are rotated by about 33° from the conformation which would have them perpendicular to the plane of the naphthalene system. To relieve the severe crowding of these bulky peri groups, the bonds C(1)–C(A1) and C(8)–C(B1) are splayed and atoms C(A1) and C(B1) are displaced to opposite sides of the naphthalene plane (Figure 4). As a result, the C(A1)–C(B1) distance is 3.108 Å compared with the C(1)–C(8) distance of 2.601 Å. The sidewise distortion plus the rotation of the phenyl rings result in a staggered conformation for the two rings. The shorter distances between atoms in the two phenyl rings are given in Table IV; they can be compared with the value of 3.4 Å estimated by Pauling[19] for the van der Waals separation for parallel aromatic systems. Both rings are planar within 0.007 Å; the dihedral angle between them is 26 ± 3°.

The fact that C–C single bonds which connect double bonds, triple bonds, or aromatic rings are substantially shorter in length than C–C single bonds between two aliphatic sites is well known. In **1** as well as in **2** and **3**, the substituent phenyl rings are severely twisted with respect to the naphthalene system and, hence, interaction between the two π systems must be minimal. Nevertheless, the aryl–aryl bond lengths are approximately the same as the values found in the planar systems biphenyl[20] and *p*-terphenyl[21] (Table V). This result accords with the view discussed at length by Dewar[22] that the relative shortening of bonds adjoining unsaturated sites is a direct consequence of differences in hybridization of the carbon bonding orbitals, and is not a result of resonance interaction between the two π systems.

General Analysis of the Molecular Distortions of the Naphthalene Nucleus in Peri-Substituted Derivatives. The perturbation introduced by steric overcrowding at the peri positions is spread throughout the naphthalene nucleus. While a perturbing force acting at a given site will be partly accommodated by local deformations, residual forces will be passed along to adjacent sites and the entire molecular framework will adjust to relieve the stress; the resultant minimum energy conformation is presumably the best compromise of bond stretchings and compressions, angle defor-



naphthalene

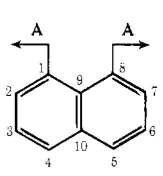
compound 1

compound 2

compound 3

Figure 4. Geometries of *peri*-diphenylnaphthalenes.

mations, and ring bucklings, perhaps slightly adjusted for interactions resulting from crystal packing. Thus, the overall changes in the geometry of the naphthalene nucleus in peri derivatives may be understood in terms of the reactions to a series of force vectors induced into the molecule at the peri positions.



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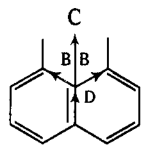

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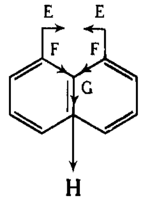

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Repulsive forces between bulky peri substituents are expected to produce vectorial forces **A**, of equal magnitude but opposite direction, acting at the sites of the substituents, **5**. Some immediate relief can be found in adjustments of the exterior bond angles at C(1) and C(8), but forces will remain that tend to separate C(1) and C(8). As a result, the bonds C(1)–C(9) and C(8)–C(9) will lengthen and the angles C(1)–C(9)–C(8), C(1)–C(2)–C(3), and C(6)–C(7)–C(8) will open. However, these adjustments—particularly the stretching of the C(1)–C(9) and C(8)–C(9) bonds—will resist the stress, and we can envision the force vectors **B** induced along these bonds, with a resultant force vector **C**, **6**. Its effect is to displace C(9) toward the top of the molecule, and to stretch the C(9)–C(10) bond. This bond, in turn, tends to resist stretching, leaving the residual force vector **D**, acting at the bottom of the molecule. This force will tend to move C(10) upward and to close the C(4)–C(10)–C(5) angle, moving C(4) and C(5) toward one another.

The opposite type of peri strain, a pinching together at the peri positions, produces an opposite chain of distortions with force vectors **E**, **F**, **G**, **H**, **7**. In a compound such as **1**, where the pinching caused by the bridging ethanyl group is at the opposite end of the molecule from the bulky phenyl groups, many of the two sets of forces act in conjunction, leading to enhanced distortions within the naphthalene nucleus; an exception is the C(9)–C(10) bond length, where the two effects tend to cancel.

Out-of-plane splay of overcrowded peri substituents induces force vectors of opposite directions at C(1) and C(8), which act to push these atoms to positions above and below the plane of the naphthalene nucleus. While these displacements should be larger than for any other atom in the naphthalene nucleus, residual forces will cause small displacements of the remaining atoms. The resultant buckling will be of opposite sense for the two six-membered rings of the naphthalene nucleus, with C(9) and C(10) remaining relatively rigid since they are common to both rings.

The relative distribution of the strain between the various in-plane and out-of-plane modes will depend on numerous factors determined by the nature of the substituents. For example, the in-plane spreading of the peri-substituent bonds may be inhibited by electronic effects in these bonds or by repulsion with the hydrogen atom (or other substituent) bonded to C(2); out-of-plane splay may be affected by the details of the geometrical fit between the peri substituents. A comparison of the structures of the three peri-diphenylnaphthalene compounds **1**, **2**, and **3** provides insight into the relative importance of these different modes.

Figure 4 summarizes the dimensions and out-of-plane displacements of **1**, **2**, and **3**, as well as of naphthalene itself, as obtained from averaging the x-ray diffraction results for naphthalene[23] with neutron diffraction results for perdeuterionaphthalene.[24]

The distortions of **2** reflect clearly the force vectors just described. Compared to naphthalene, the bond angle C(1)–C(9)–C(8) is enlarged by nearly 5°, the angle C(4)–C(10)–C(5) is closed by over 2°, and the angle C(1)–C(2)–C(3) is opened by 1.4°; the bond C(9)–C(10) is lengthened by 0.03 Å and the bonds of the types C(1)–C(2) and C(1)–C(9) are lengthened by lesser amounts. The exocyclic bonds to the peri substituents are splayed in-plane by about 5° and out-of-plane by about 2°. Despite these distortions, stress clearly remains, for the nonbonded contact of 2.99 Å between C(A1) and C(B1) is uncomfortably short.

The addition of a pinching group at the 4,5 positions, as in **1**, results in an enhancement of most of the distortions in **2**.

Table III. Carbon–Hydrogen Bond Distances and Angles of *peri*-Diphenylacenaphthene[a,b]

Acenaphthene Ring

Bond lengths, Å		Bond angles, deg			
C(2)–H(2)	1.00	C(1)–C(2)–H(2)	117.9	C(3)–C(2)–H(2)	118.1
C(3)–H(3)	1.01	C(2)–C(3)–H(3)	118.6	C(4)–C(3)–H(3)	123.0
C(6)–H(6)	1.02	C(5)–C(6)–H(6)	121.3	C(7)–C(6)–H(6)	120.3
C(7)–H(7)	1.01	C(6)–C(7)–H(7)	117.9	C(8)–C(7)–H(7)	118.0
C(11)–H(11)	1.01	C(4)–C(11)–H(11)	110.4	C(12)–C(11)–H(11)	112.0
C(11)–H(11′)	1.00	C(4)–C(11)–H(11′)	110.2	C(12)–C(11)–H(11′)	112.8
C(12)–H(12)	1.04	C(5)–C(12)–H(12)	110.9	H(11)–C(11)–H(11′)	106.3
C(12)–H(12′)	1.01	C(5)–C(12)–H(12′)	109.5	C(11)–C(12)–H(12)	113.4
				C(11)–C(12)–H(12′)	113.3
				H(12)–C(12)–H(12′)	104.8
				C(4)–C(11)–C(12)	105.2
				C(5)–C(12)–C(11)	104.9

Phenyl Rings

Bond lengths, A			Bond angles, deg					
	A	B		A	B		A	B
C(2)–H(2)	1.01	1.00	C(1)–C(2)–H(2)	119.2	118.9	C(3)–C(2)–H(2)	120.4	120.6
C(3)–H(3)	1.02	1.01	C(2)–C(3)–H(3)	119.6	119.2	C(4)–C(3)–H(3)	119.8	119.9
C(4)–H(4)	1.03	1.03	C(3)–C(4)–H(4)	120.4	120.3	C(5)–C(4)–H(4)	120.1	120.2
C(5)–H(5)	1.00	1.02	C(4)–C(5)–H(5)	121.7	120.0	C(6)–C(5)–H(5)	118.0	120.1
C(6)–H(6)	1.00	0.99	C(5)–C(6)–H(6)	119.9	121.1	C(1)–C(6)–H(6)	119.3	117.8

[a] Esd's for C–H bond distances are about 0.01–0.02 Å. [b] Esd's for C–C–H bond angles are about 0.7° and esd's for H–C–H angles are about 1.0°.

Table IV. Distances Between Carbons of the Adjacent Phenyl Rings, in Å

		Ring A		
		1	2	6
	1	3.108	3.991	3.039
Ring B	2	3.041	3.430	3.257
	6	3.990	4.929	3.427

Table V. Aryl–Aryl Bond Lengths

Compd	Inter-ring dihedral angle, deg	Aryl–Aryl bond length, Å
1,8-Diphenylnaphthalene	67	1.492 ± 0.004
peri-Diphenylacenaphthene	57	1.490 ± 0.002
1,4,5,8-Tetraphenylnaphthalene	58	1.504 ± 0.004
Biphenyl	0	1.497 ± 0.003
p-Terphenyl	0	1.496 ± 0.004

An exception is the central C(9)–C(10) bond; here, the two stresses act on atoms C(9) and C(10) in the same direction and the resulting bond length in **1** is close to that found in naphthalene. At the same time, C(9) and C(10) are displaced in the direction C(10) → C(9) by 0.19 and 0.18 Å, respectively, relative to the position of the pairs C(2), C(7) and C(3), C(6). The twist of 2.3° about the C(11)–C(12) bond, which slightly relieves the eclipsing of the protons of the methylene groups, acts cooperatively with the out-of-plane splaying of the phenyl groups (~11°) to induce appreciable out-of-plane distortions of the naphthalene nucleus. Because both in-plane and out-of-plane distorting forces at the 4,5 end of the molecule act in cooperation with those at the 1,8 positions, the phenyl groups attain greater steric relief, and the C(A1)···C(B1) separation is a more comfortable 3.11 Å.

With **3**, the in-plane distorting forces at the two ends of the naphthalene group tend to cancel one another and the bond distances and angles are close to those found in naphthalene itself; an exception is the C(9)–C(10) bond, where both stresses act to produce a high degree of stretching. Because **3** cannot find much relief by in-plane distortions, the out-of-plane splaying of the phenyl groups is greatly magnified to about 34° and, once again, the splaying at the 4,5 positions acts cooperatively with that at the 1,8 positions to produce relatively large out-of-plane distortions of the naphthalene nucleus.

The question of the ease of rotation about the interannular C–C bonds of 1,8-diphenylnaphthalene reported by House and co-workers[5a] will be discussed in some detail in a later paper. For the present, we will give only a qualitative argument as to why this should be so, based on the x-ray structures. Attempts to assess the magnitude of the barrier with conventional Corey–Pauling–Koltun models or the like lead to the expectation that such rotation would be virtually impossible. The difference between the models and the molecules as revealed by x-ray diffraction is the way the axes of the phenyl rings become nonparallel as the result of the strong nonbonded interaction between C(A1) and C(B1). This is clearly shown for **1** in Figure 3 and for **2** in Figure 5 (wherein the drawing also reflects the distortions of C(1) and C(8) from the normal positions in naphthalene itself). Now, when the phenyl rings are allowed to splay to opposite sides, the model constructed as to Figure 5 can be twisted to allow simulation of a rotation transition state without prohibitive further contortions, as shown in broadside view in Figure 6a, and in top view in Figure 6b. The general conclusion is that the ground-state strain is sufficiently great as to allow the transition state for rotation to be achieved much more readily than would be the case for simple ortho-substituted biphenyls where the ground-state interactions are small or even nonexistent.

^{1}H NMR Studies of *peri*-Diphenylacenaphthene (1). The ^{1}H NMR spectrum of **1** is strikingly simple. At 60 MHz,

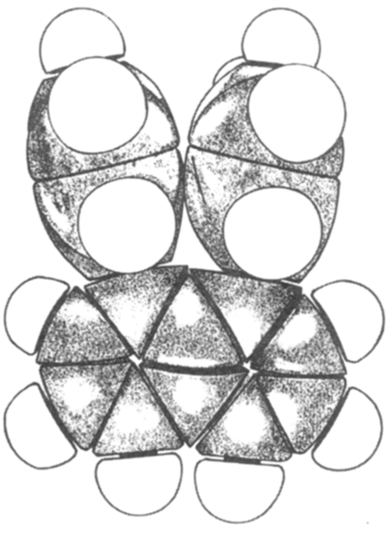

Figure 5. CPK model of **2**, modified to reflect the changes in ring-bond angles at C(1) and C(8) resulting from repulsions between the phenyl groups.

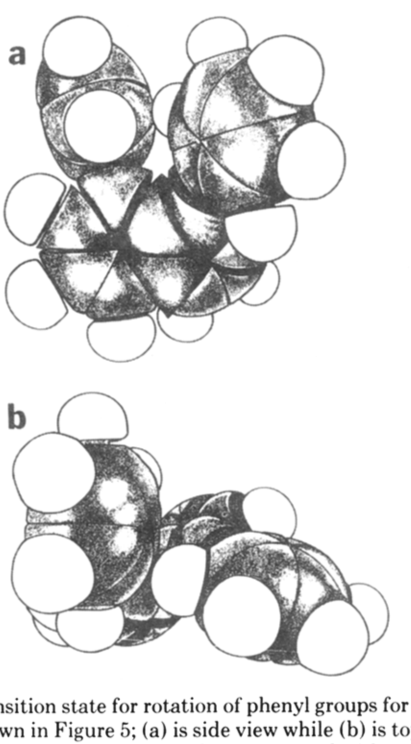

Figure 6. Transition state for rotation of phenyl groups for the CPK model of **2** shown in Figure 5; (a) is side view while (b) is top view. A model of the transition state cannot be constructed with unmodified CPK models.

the spectrum consists of three sharp singlets (δ 7.30, 6.87, 3.43; 4:10:4). The spectrum indicates that the conformation of **1** in solution is similar to that found in the crystal. The argument for this conclusion follows. In the first place, replacement of a proton on an aromatic ring by a methyl or ethyl group gives rise to very small chemical-shift differences between remaining protons. Thus, the aryl portions of the spectra of toluene and ethylbenzene[25] are in each case a single sharp peak at 60 MHz. However, replacement by a substituent having electronic properties quite different from a proton usually results in a more complex aromatic proton signal. Diaryl systems in which the rings are relatively free to approach coplanarity[26] exhibit highly split multiplets for the aryl protons, as may be seen[27] in the spectra of biphenyl, *m*-terphenyl, *p*-terphenyl, and *trans*-stilbene. However, the aryl protons of systems which are sterically constrained from assuming a nearly coplanar conformation give a sharp single peak, as with *o*-terphenyl and *cis*-stilbene.[28] The difference is the result of the combination of a resonance interaction and a larger ring current shift for the more coplanar systems.[29,30]

Thus, the sharp singlet of the phenyl protons of **1** at δ 6.87 is indicative of the perpendicularity of the system and may be compared to the spectrum of biphenyl, which shows a complex multiplet. The sharp singlet at δ 7.30 from the four naphthalene protons of **1** may be contrasted with the protons of *p,p'*-bitolyl which give an A_2B_2 pattern having a chemical shift difference of 14 Hz at 60 MHz. The phenyl peak of *peri*-diphenylacenaphthene is shifted 0.5 ppm upfield from the phenyl signal of 1-phenylnaphthalene because of the ring current of the adjacent peri phenyl ring, consistent with a parallel conformation of the two phenyl rings. The shift difference is nearly the same as for the phenyl-ring protons of 1-phenylnaphthalene and 1,8-diphenylnaphthalene,[31] and also of *p*-xylene[32] and [2.2]paracyclophane.[33]

The distortions produced in the naphthalene ring do not seem to have any appreciable effect on the chemical shifts of the naphthyl protons, which come into resonance very near to the β protons of naphthalene itself[34] (δ 7.30 vs. 7.38).

Registry No.—**1,** 57620-87-8; *peri*-diiodoacenaphthene, 55143-88-9.

References and Notes

(1) (a) Supported by the National Science Foundation; (b) NDEA Title IV Fellow, 1971–1974.

(2) A valuable review was prepared by V. Balasubramaniyan, *Chem. Rev.*, **66,** 567 (1966).

(3) D. L. Fields and T. H. Regan, *J. Org. Chem.* **36,** 2986 (1971).

(4) J.-B. Robert, J. S. Sherfinski, R. E. Marsh, and J. D. Roberts, *J. Org. Chem.* **39,** 1152 (1974), and references cited therein.

(5) (a) H. House, W. J. Campbell, and M. Gall, *J. Org. Chem.*, **35,** 1815 (1970); (b) J. E. Anderson, R. Franck, and W. Mandella, *J. Am. Chem. Soc.*, **94,** 4608 (1972).

(6) R. A. Ogilvie, Ph.D. Thesis, Massachusetts Institute of Technology, 1971.

(7) P. G. Evrard, P. Piret, and M. Van Meerssche, *Acta Crystallogr., Sect. B,* **28,** 497 (1972).

(8) (a) R. J. P. Corriu and J. P. Masse, *J. Chem. Soc., Chem. Commun.*, 144 (1972); (b) R. L. Clough, P. Mison, and J. D. Roberts, *J. Org. Chem.*, submitted.

(9) G. Morgan and H. Stanley, *J. Chem. Ind.*, **43,** 343 (1924).

(10) A. Karishin and D. Kustol, *J. Gen. Chem. USSR* (*Engl. Transl.*) **34,** 994 (1964).

(11) All calculations were carried out on an IBM-370/155 computer under the CRYM system of crystallographic programs.

(12) (a) W. H. Zachariasen, *Acta Crystallogr.*, **16,** 1139 (1963); (b) A. C. Larson, *ibid.*, **23,** 664 (1967).

(13) The carbon atoms are numbered according to the naphthalene and not the acenaphthene numbering system in order to facilitate comparison with other peri compounds; C(1) and C(8) carry the two phenyl groups and C(4) and C(5) are connected to the ethylene bridge. According to the standard numbering system for acenaphthene, in which the carbons of the bridging group are numbered 1 and 2, compound **1** would be 5,6-diphenylacenaphthene.

(14) The direction cosines, relative to *a, b,* and *c*, for this plane are 0.7840, 0.3257, 0.2197.

(15) A. Bondi, *J. Phys. Chem.*, **68,** 441 (1964), and references cited therein.

(16) (a) R. A. Bonham and L. S. Bartell, *J. Am. Chem. Soc.*, **81,** 3491 (1959); (b) L. H. Jensen and A. J. Mabis, *Acta Crystallogr.*, **21,** 770 (1966).

(17) T. F. Koetzle, M. N. Frey, M. S. Lehmann, and W. C. Hamilton, *Acta Crystallogr., Sect. B,* **29,** 2571 (1973).

(18) J. L. Crawford and R. E. Marsh, *Acta Crystallogr., Sect. B,* **29,** 1238 (1973).

(19) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, pp 260–262.

(20) G. B. Robertson, *Nature* (*London*), **191,** 593 (1961).

(21) H. M. Rietveld, E. N. Maslen, and C. J. B. Clews, *Acta Crystallogr., Sect. B,* **26,** 693 (1970).

(22) M. J. S. Dewar, "Hyperconjugation", Ronald Press, New York, N.Y., 1962, pp 48–57.

(23) D. W. J. Cruikshank, *Acta Crystallogr.*, **10,** 504 (1957).

(24) G. S. Pauley and E. A. Yeats, *Acta Crystallogr., Sect. B,* **25,** 2009 (1969).

(25) "Varian NMR Spectra Catalogue", Varian Associates, Palo Alto, Calif., 1962, No. 157, 505.

(26) The dihedral angle of biphenyl in solution does not seem wholly settled. Depolarization of Rayleigh scattered light is reported to give values of 24 and 31° [I. A. Bogdanov and M. F. Vuks, *Ser. Fiz. Khim.*, **3,** 46 (1965); A. Unanve and P. Bothorel, *Bull. Soc. Chim. Fr.*, **5,** 1640 (1966)]; ultraviolet spectra suggest an angle of about 20° [H. Suzuki, *Bull. Chem. Soc. Jpn.*,

32, 1340 (1959)] while molar Kerr constants [J. Y. H. Chan, C. G. Le Fevre, and R. J. W. Le Fevre, *J. Chem. Soc.*, 2666 (1959)] and magnetic anisotropy measurements [C. L. Cheng, D. S. N. Murthy, and G. L. D. Ritchie, *J. Chem. Soc., Faraday Trans. 2*, 1679 (1972)] have led to calculated values of 0°. The barrier to rotation about the aryl–aryl bond is expected to be low, and essentially free rotation is usually assumed at room temperature.
(27) "Varian NMR Spectra Catalogue", No. 289, 669, 671, 306.
(28) "Varian NMR Spectra Catalogue", No. 670, 305.
(29) M. Katayama, S. Fujiwara, H. Suzuki, Y. Nagai, and O. Simamura, *J. Mol. Spectrosc.*, **5**, 85 (1960).
(30) R. J. Kurland and W. B. Wise, *J. Am. Chem. Soc.*, **86**, 1877 (1964).
(31) H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963).
(32) "Varian NMR Spectra Catalogue", No. 305.
(33) D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Am. Chem. Soc.*, **85**, 1088 (1963).
(34) "Sadtler Standard Spectra Catalogue", Sadtler Research Laboratories, 1966, No. 62.

Hypervalent Organoiodine. Crystal Structure of Phenylhydroxytosyloxyiodine

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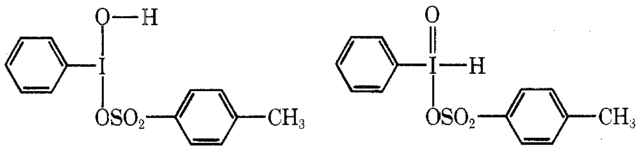
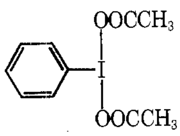
Phenylhydroxytosyloxyiodine was subjected to x-ray analysis and was found to exhibit the three-coordinate iodine(III) structure **1a** in the solid state. The structure of **1a** was refined, and the positions of all hydrogen atoms were determined. H_1 is clearly bonded to O_1 and not to iodine as the four-coordinate iodine(V) structure **1b** would demand.

A number of compounds believed to contain a hydroxy group bound to trivalent iodine are known.[1-8] One such substance, phenylhydroxytosyloxyiodine (**1**), reported in 1970 by Neiland and Karele, is accessible through the action of toluenesulfonic acid on iodosobenzene diacetate (**2**).[9] We wondered about the possibility that **1** may prefer the four-coordinate iodine(V) structure, **1b**, over the three-coordinate iodine(III) structure, **1a**, which had been assigned to it and that such "tautomerism" may be general among compounds thought to contain the >I–OH moiety. We drew analogy from organophosphorus chemistry. For example, dialkylphosphonates may exhibit the four-coordinate phosphorus(V) structure, **3**, as well as the corresponding three-coordinate phosphorus(III) structure, **4**.[10]



a b

1



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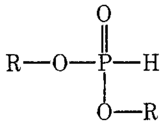

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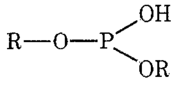

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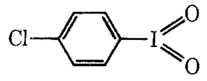

5

A spectroscopic analysis of **1** does not lead to a clear-cut choice between **1a** and **1b**. The infrared spectrum exhibits a strong absorption band which maximizes at 3.25 μ (~3100 cm^{-1}) and extends from 2.9 to 3.9 μ. This may be due to -O-H stretching in **1a**, but, since **1** possesses both aromatic and aliphatic C–H bonds, such an assignment is uncertain. The ^1H NMR spectrum of **1** (Me_2SO-d_6) exhibits a singlet at ~δ 9 which belongs to an exchangeable hydrogen atom. There is, however, no reason to presume that hydrogen–deuterium exchange will be possible for **1a** but not for **1b**, especially since **1b** may isomerize to **1a** in solution.

Results and Discussion

Because of this structural dichotomy and because structural studies on hypervalent organoiodine compounds are uncommon, compound **1** was subjected to single-crystal x-ray analysis. The results of our study are summarized in Tables I and II and Figure 1.

It seems clear that, at least in the solid state, phenylhydroxytosyloxyiodine exhibits structure **1a**, a conclusion which rests on the following considerations: (1) The I–O_1 bond distance in **1** was found to be 1.940 Å, consistent with a single bond distance of 1.99 Å computed from covalent radii. *p*-Chloroiodoxybenzene (**5**) has two iodine–oxygen "double bonds", and they exhibit lengths of 1.60 and 1.65 Å.[11] (2) All hydrogen atoms were located in a difference Fourier, and all atoms were included in least-squares refinements. The distance from O_1 to the "tautomeric" hydrogen atom was found to be 0.75 Å while the distance from iodine to the same hydrogen atom was found to be 2.17 Å. This result is consistent with an O–H bond instead of a I–H bond. (3) The geometry about iodine in **1** is T-shaped (refer to the O_1–I–O_2, O_1–I–C, and O_2–I–C bond angles), a configuration which has been observed with other trivalent organoiodine compounds.[12-14] Also, it seems likely that structure **1b** would be tetrahedral about the iodine atom.

It is noteworthy that the I–O_2 bond distance in **1a** (2.473 Å) is significantly longer than the computed covalent single bond distance of 1.99 Å. At the same time, the O_2–S bond distance (1.467 Å) is significantly shorter than the computed distance of 1.70 Å. These facts, coupled with the observation that all three sulfur–oxygen bonds are comparable in length, indicate that the I–O_2 bond in **1a** may possess some ionic character. We know of only one other compound with an >I–OH unit which has been subjected to x-ray analysis, and it is similar