# Structural Distortions in Diiodine-Substituted Unsaturated Hydrocarbons**

**Hans Bock,* Mark Sievert, and Zdenek Havlas**

*Dedicated to Professor Heribert Offermanns on the occasion of his 60th birthday*

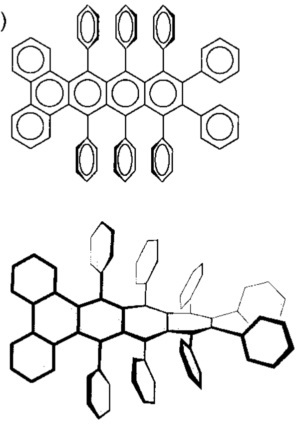
**Abstract:** 1,10-Diiodophenanthrene, prepared for the first time by reacting $I_2$ with dilithiophenanthrene, has a twist angle $\omega(I\cdots C-C\cdots I) = 63^\circ$ between the two iodine centers and a distance $d_{I\cdots I} = 3.61$ Å, which amounts to only 84% of the sum of van der Waals radii, $2r_I^{vdW} = 2 \times 2.15 = 4.30$ Å. Based on an extensive literature search for distortions of carbon skeletons by repulsion between overlapping iodine substituents, the low-temperature structures of 2,2′-diiodobiphenyl ($\omega = 85^\circ$, $d_{I\cdots I} = 4.35$ Å, 101% of $2r_I^{vdW}$) and 1,8-diiodonaphthalene ($\omega = 2^\circ$ to $17^\circ$, $d_{I\cdots I} = 3.51-3.54$ Å, 82% of $2r_I^{vdW}$) have also been determined. Density functional B3LYP calculations with 6-31G** basis sets and 31G* effective pseudopotentials for iodine provide information on an unexpectedly balanced charge distribution, leading to estimates of about 30 kJ mol$^{-1}$ for the I/I repulsion and of about 10 kJ mol$^{-1}$ for the reduced π delocalization in the extremely twisted skeleton of 1,10-diiodophenanthrene.

**Keywords:** arenes · density functional calculations · interatomic repulsion · iodine · skeletal distortion

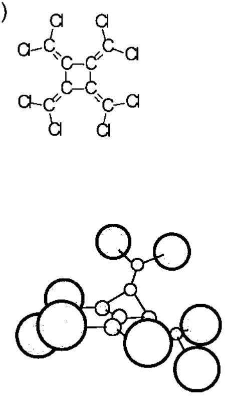
## Introduction

**Molecular distortion due to nonbonded substituent interactions**: Sterically overcrowded and therefore structurally distorted molecules or molecular ions have attracted the attention of chemists for many years.[2] Numerous such species have been reported, of which we have selected one π- and one electron-pair-perturbed example for this introduction. The recently published structure of octaphenyldibenzo[*a,c*]naphthacene (**A**) shows a 105° twist along the long hydrocarbon axis,[3] and octachlorotetraradialene (**B**), structurally characterized in 1970,[4] is a severely distorted four-membered ring. In contrast to π interactions, well-investigated recently due to their biochemical implications,[5] the repulsive σ-type interactions between one-center substituents such as the halogens still need further exploration.

(A)



(B)



For qualitative estimates of the space filled by substituents, which can provide kinetic stabilization of thermodynamically stable molecules generated in the gas phase under unimolecular conditions but that rapidly polymerize on condensation,[6] often the interference, interaction, or van der Waals radii[7] are considered. They are derived from ionic radii or molecular structures,[7a] de Broglie wavelengths, collision cross-sections, or critical-point data,[7b] and from force-field calculations.[7c] Their angle- and direction-dependent[7a,d] values are occasionally overestimated.[7e] According to a more general definition, the van der Waals volume of a molecule cannot be penetrated by that of another one at thermal energies corresponding to room temperature.[7b]

Some frequently used literature values for hydrogen and halogen centers[7a,f] are compared with essential C···C distances in the molecular skeletons of the unsaturated hydrocarbons phenanthrene, biphenyl, and naphthalene, the structural distortions of which we investigate here (Scheme 1 A).

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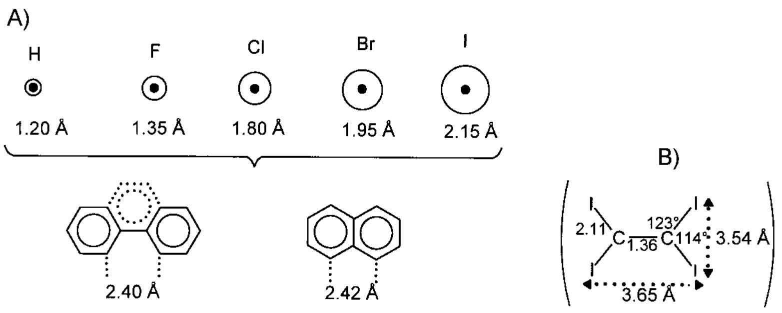
[**] Interactions in Molecular Crystals, Part 137. Part 136: ref. [1].



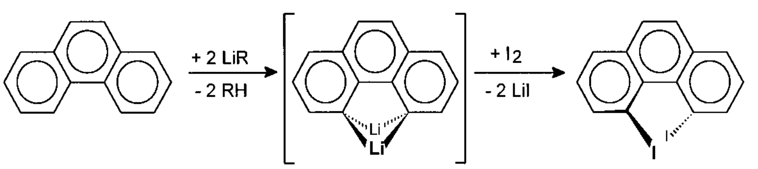
Scheme 1. A) Some frequently used literature values for hydrogen and halogen van der Waals radii compared with essential C···C distances in the molecular skeletons of the unsaturated hydrocarbons phenanthrene, biphenyl, and naphthalene, and B) C···I distances and selected angles in planar tetraiodoethene.

Despite the frequently demonstrated usefulness of interference radii for qualitative estimates of structures containing bulky groups,[2] some caution is advisable even for single-center substituents: The structure of planar tetraiodoethene (Scheme 1 B), determined by gas-phase electron diffraction,[8] has distances of 3.65 and 3.54 Å between vicinal and geminal iodine centers, which are considerably exceeded by the sum of their interference radii, $2r_{I}^{vdW} = 2 \times 2.15 = 4.30$ Å, and indicate that for groups $CHal_2$, therefore, the assumption of spherical electron-density distributions around the individual halogen centers[7a,d] is obviously unjustified.

## Results and Discussion

Our investigations started with the synthesis of the unknown 1,10-diiodophenanthrene[9] by a well-known dilithiation route[10] (Scheme 2 and Experimental Section). The structure determination revealed a surprising twisting of the phenanthrene skeleton by an interiodine angle of 63° and stimulated the preparation and crystal growth of both 2,2′-diiodobiphenyl and of 1,8-diiodonaphthalene, the structural data for which are not listed so far in the Cambridge Structural Database. The hydrocarbon skeletal distortions due to repulsive interactions between overlapping iodine substituents are discussed based on density functional B3LYP calculations with 6-31G** basis sets, which for the iodine centers were completed by effective pseudopotential 31G* functions (Experimental Section).

**Crystal structures**: The structures of the diiodohydrocarbons investigated will be presented in the sequence of perturbations: Beginning with 1,10-diiodophenanthrene, the removal of the CCCC bridge in the central six-membered ring generates the rotationally flexible 2,2′-diiodobiphenyl, and further ring condensation 1,8-diiodonaphthalene, the in-plane distortions of which will also be discussed.



Scheme 2. Synthesis of 1,10-diiodophenanthrene by dilithiation.

*1,10-Diiodophenanthrene*: The compound crystallizes in the triclinic space group $P\bar{1}$ with Z = 4 molecules in the unit cell (Figure 1). The structure contains two crystallographically independent molecules. The 1,10-diiodophenanthrene molecules form alternating stacks both in *x* (Figure 1, A) and *y* directions (Figure 1, B) with an angle of 74° between them. The interplanar distances between the idealized molecular planes amount to 3.62 (0.006) Å along the *x* stack and 3.74 (0.007) Å along the *y* one, exceeding the double van der Waals π radius of 3.40 Å[7a] by 0.22 and 0.34 Å, respectively. This is presumably a result of the repulsion between the bulky iodine substituents, for which a shortest intermolecular distance of 4.10 Å is determined.

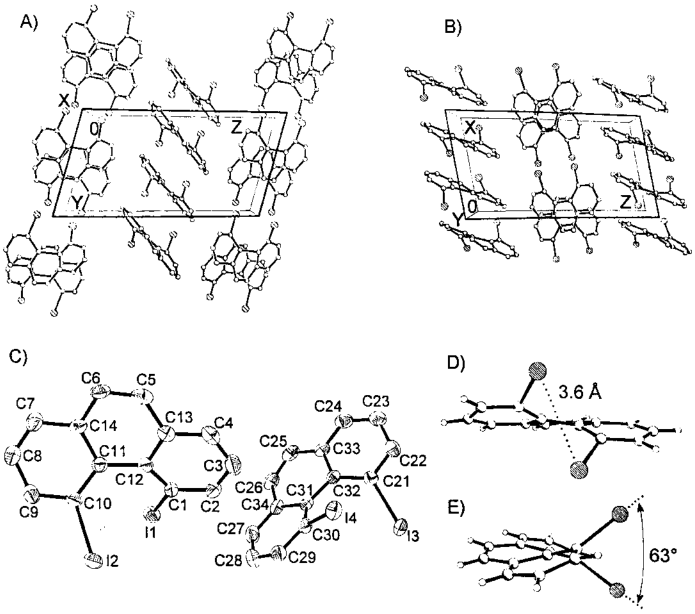


Figure 1. Crystal structure of 1,10-diiodophenanthrene at 150 K: A) unit cell (triclinic, $P\bar{1}$, $Z = 4$) viewed along the *x* and B) the *y* axes, C) structures of the two crystallographically independent molecules with numbering (thermal ellipses drawn at the 50 % probability level); D) front and E) side view (● = I; ○ = C; ∘ = H).

The two crystallographically independent molecules exhibit almost identical structural parameters, as expected (Table 1). The structures are dominated by the torsional distortion due to the I1/I2 or I3/I4 repulsive interactions at a distance of 3.60 Å, which is about 16 % shorter than two van der Waals radii of iodine, $2r_{I}^{vdW} = 2 \times 2.15 = 4.3$ Å[7a] (Scheme 1). The torsion around the C–C bond in the central region of 1,10-diiodophenanthrene amounts to 63° (!) with respect to the axes of the C–I bonds. This rather large skeletal distortion is best illustrated by the considerable distance of

Table 1. Selected bond lengths [Å] and angles [°] of 1,10-diiodophenanthrene (see Figure 1 for numbering).

| | | | | | |
|---|---|---|---|---|---|
| I(1)-C(1) | 2.108 (4) | C(7)-C(14) | 1.404 (6) | C(25)-C(26) | 1.348 (6) |
| I(2)-C(10) | 2.106 (4) | C(9)-C(10) | 1.387 (6) | C(25)-C(33) | 1.437 (6) |
| I(3)-C(21) | 2.101 (4) | C(10)-C(11) | 1.427 (6) | C(26)-C(34) | 1.433 (6) |
| I(4)-C(30) | 2.112 (4) | C(11)-C(14) | 1.434 (5) | (C27)-C(28) | 1.373 (5) |
| C(1)-C(2) | 1.392 (6) | C(11)-C(12) | 1.463 (5) | C(27)-C(34) | 1.411 (6) |
| C(1)-C(12) | 1.418 (5) | C(12)-C(13) | 1.414 (5) | C(29)-C(30) | 1.393 (6) |
| C(3)-C(4) | 1.382 (7) | C(21)-C(22) | 1.396 (5) | C(30)-C(31) | 1.418 (5) |
| C(4)-C(13) | 1.406 (6) | C(21)-C(32) | 1.421 (5) | C(31)-C(34) | 1.425 (5) |
| C(5)-C(6) | 1.347 (7) | C(23)-C(24) | 1.373 (6) | C(31)-C(32) | 1.459 (5) |
| C(5)-C(13) | 1.435 (6) | C(24)-C(33) | 1.404 (6) | C(32)-C(33) | 1.435 (5) |
| C(6)-C(14) | 1.435 (6) | | | | |

| | | | |
|---|---|---|---|
| C(2)-C(1)-C(12) | *121.0 (4)* | C(22)-C(21)-C(32) | *120.7 (4)* |
| C(2)-C(1)-I(1) | *113.9 (3)* | C(22)-C(21)-I(3) | *114.6 (3)* |
| C(12)-C(1)-I(1) | *123.3 (3)* | C(32)-C(21)-I(3) | *123.2 (3)* |
| C(1)-C(2)-C(3) | *120.2 (4)* | C(23)-C(22)-C(21) | *120.7 (4)* |
| C(4)-C(3)-C(2) | *118.6 (4)* | C(24)-C(23)-C(22) | *119.8 (4)* |
| C(3)-C(4)-C(13) | *121.1 (4)* | C(23)-C(24)-C(33) | *120.6 (4)* |
| C(9)-C(10)-C(11) | *121.6 (4)* | C(29)-C(30)-C(31) | *121.2 (4)* |
| C(9)-C(10)-I(2) | *114.5 (3)* | C(29)-C(30)-I(4) | *113.9 (3)* |
| C(11)-C(10)-I(2) | *122.6 (3)* | C(31)-C(30)-I(4) | *123.1 (3)* |
| C(10)-C(11)-C(14) | *115.3 (3)* | C(30)-C(31)-C(34) | *116.2 (3)* |
| C(10)-C(11)-C(12) | *126.8 (3)* | C(30)-C(31)-C(32) | *126.4 (3)* |
| C(14)-C(11)-C(12) | *117.6 (3)* | C(34)-C(31)-C(32) | *117.3 (3)* |
| C(13)-C(12)-C(1) | *116.6 (4)* | C(21)-C(32)-C(33) | *116.0 (3)* |
| C(13)-C(12)-C(11) | *117.7 (3)* | C(21)-C(32)-C(31) | *126.0 (3)* |
| C(1)-C(12)-C(11) | *125.6 (3)* | C(33)-C(32)-C(31) | *117.8 (3)* |

0.43 Å between a C center and the idealized plane resulting for the twisted phenanthrene π system. The C–I bond lengths of 2.11 (0.004) Å are normal,[11] but some unusual angle deviations are observed (Table 1). For instance, the angles C-C-I are enlarged to 123 (0.3)° and the angles C10-C11-C12 and C30-C31-C32 to 126 (0.3)°. In the central phenanthrene ring, the usual bond alternation is more pronounced, with short distances C5–C6 and C25–C26 of only 1.35(0.007) Å and rather long ones C11–C12 as well as C31–C32 of 1.46(0.005) Å (Table 1).

*2,2′-Diiodobiphenyl*: The known compound[10] is synthesized analogously to the method of Scheme 2 by reacting the dilithium biphenyl with elemental iodine (Experimental Section) and crystallizes in the orthorhombic space group *P*bca with $Z = 8$ molecules in the unit cell (Figure 2) stacked along the *y* direction (Figure 2 A and B).

The crystal packing of the severely twisted 2,2′-diiodobiphenyl molecules with their space-filling iodine substituents (Figure 2 A) exhibits stacks, for which the closest intermolecular distance is determined to be only 3.89 (0.009) Å, that is, 0.31 Å smaller than the double van der Waals radius of iodine (Scheme 1). The torsion angle of 85° around the central C–C bond in 2,2′-diiodobiphenyl (Figure 2 E), which exhibits a normal length of 1.5 (0.005) Å[11] (Table 2), separates the two iodine centers by a distance of 4.35 (0.009) Å. The phenyl rings form ipso angles of 118° at the C–C connection centers and do not show any significant distortions. Electron diffraction in the gas phase yields a slightly lower torsion angle of 79°.[12]

Table 2. Selected bond lengths [Å] and angles [°] of 2,2′-diiodobiphenyl (for numbering of the centers, see Figure 2).

| | | | | | |
|---|---|---|---|---|---|
| I(1)-C(1) | 2.107 (4) | C(3)-C(4) | 1.384 (7) | C(7)-C(8) | 1.368 (7) |
| I(2)-C(10) | 2.103 (4) | C(4)-C(5) | 1.379 (6) | C(8)-C(9) | 1.377 (7) |
| C(1)-C(12) | 1.386 (5) | C(5)-C(12) | 1.394 (5) | C(9)-C(10) | 1.389 (5) |
| C(1)-C(2) | 1.402 (6) | C(6)-C(7) | 1.390 (6) | C(10)-C(11) | 1.384 (5) |
| C(2)-C(3) | 1.369 (6) | C(6)-C(11) | 1.392 (5) | C(11)-C(12) | 1.500 (5) |

| | | | |
|---|---|---|---|
| C(12)-C(1)-C(2) | *120.7 (4)* | C(8)-C(9)-C(10) | *119.0 (4)* |
| C(12)-C(1)-I(1) | *120.5 (3)* | C(11)-C(10)-C(9) | *122.0 (4)* |
| C (2)-C(1)-I(1) | *118.7 (3)* | C(11)-C(10)-I(2) | *120.3 (3)* |
| C(3)-C(2)-C(1) | *119.6 (4)* | C(9)-C(10)-I(2) | *117.7 (3)* |
| C(2)-C(3)-C(4) | *120.5 (4)* | C(10)-C(11)-C(6) | *117.8 (4)* |
| C(5)-C(4)-C(3) | *119.6 (4)* | C(10)-C(11)-C(12) | *122.0 (3)* |
| C(4)-C(5)-C(12) | *121.3 (4)* | C(6)-C(11)-C(12) | *120.2 (3)* |
| C(7)-C(6)-C(11) | *120.3 (4)* | C(1)-C(12)-C(5) | *118.2 (4)* |
| C(8)-C(7)-C(6) | *120.6 (4)* | C(1)-C(12)-C(11) | *122.0 (3)* |
| C(7)-C(8)-C(9) | *120.3 (4)* | C(5)-C(12)-C(11) | *119.8 (3)* |

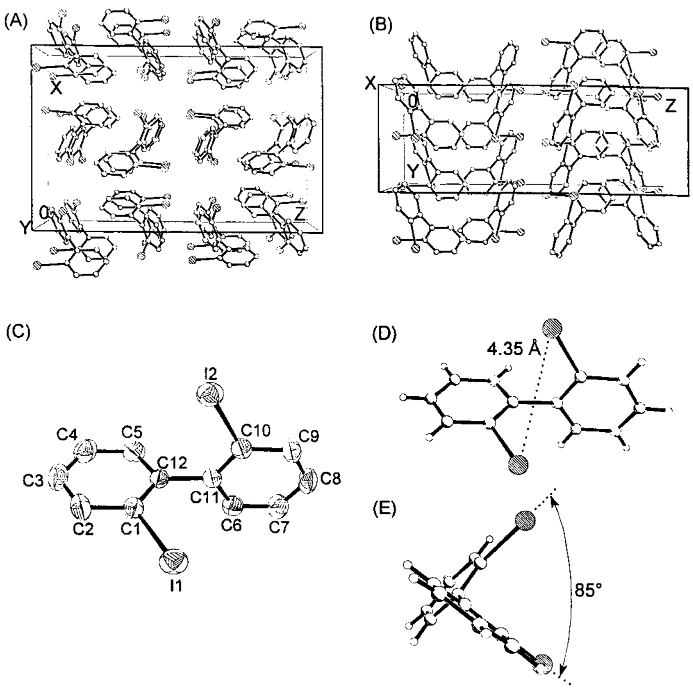
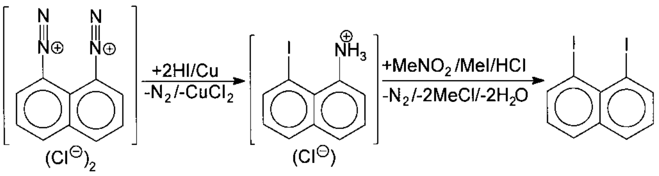


Figure 2. Crystal structure of 2,2′-diiodobiphenyl at 200 K: (A) unit cell (orthorhombic, *P*bca, $Z = 8$) viewed along the *y* and (B) the *x* axes, (C) molecular structure with numbering of the centers (thermal ellipses drawn at the 50 % probability level; (D) front and (E) side view (● = I; ○ = C; ○ = H).



Scheme 3. Synthesis of 1,8-diiodonaphthalene (1910) by diazotation of 1,8-diaminonaphthalene and its two-step iodide decomposition.

*1,8-Diiodonaphthalene*: The compound was synthesized as far back as 1910 by diazotation of 1,8-diaminonaphthalene and its two-step iodide decomposition (Scheme 3,[13] Experimental Section). For the orange-brown needles recrystallized from methanol, a rather complex structure in the triclinic space group $P\bar{1}$ with $Z = 12$ molecules in the unit cell is determined (Figure 3), which contains no less than six (!) crystallographically independent 1,8-diiodonaphthalenes (Figure 3 C).

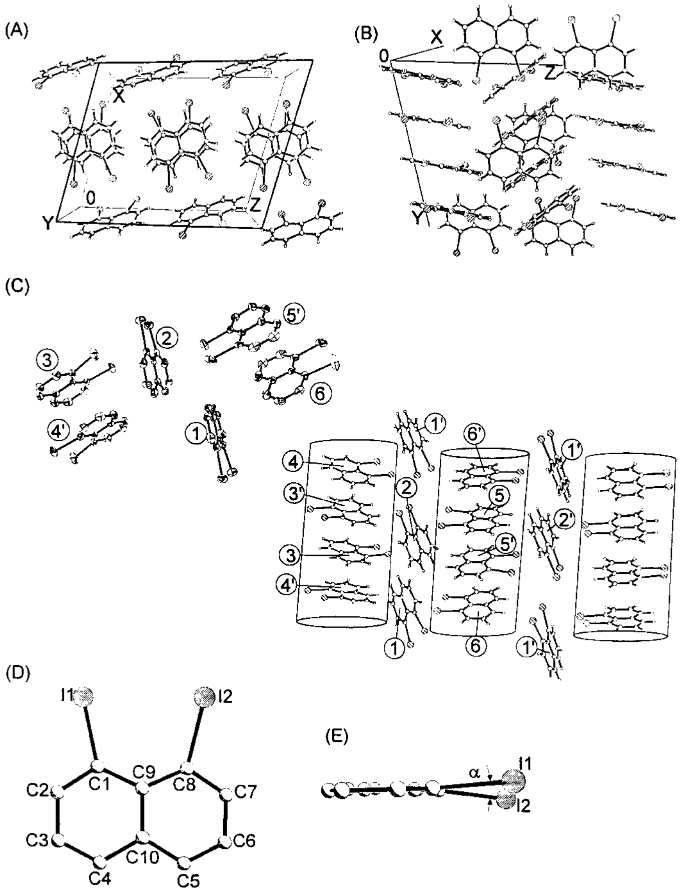
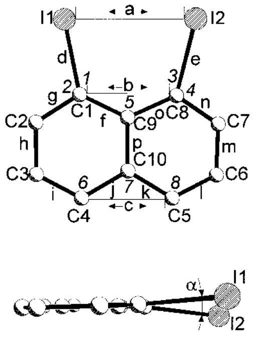


Figure 3. Crystal structure of 1,8-diiodonaphthalene at 200 K: (A) unit cell (triclinic $P\bar{1}$, $Z=12$) viewed along the $y$ axis, (B) side view of the staples, (C) the six crystallographically independent molecules (thermal ellipses drawn at the 50 % probability level) as well as their location within the stacks and the molecular structure viewed (D) from top and (E) in the hydrocarbon plane, with angles $\alpha$ between 2° and 17° (Table 3). (● = I; ○ = C; ∘ = H).

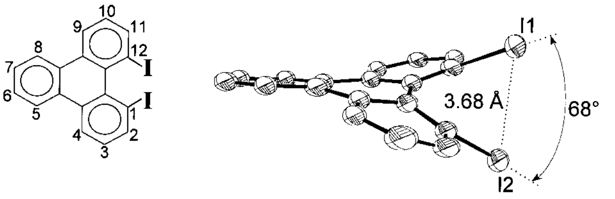
Table 3. Selected bond lengths [Å], angles [°] and intramolecular distances [Å] of the six crystallographically independent 1,8-diiodonaphthalene molecules (for indexing see diagrams).



| Molecule | ① | ② | ③ | ④ | ⑤ | ⑥ |
|---|---|---|---|---|---|---|
| Bonds [Å] | | | | | | |
| d | 2.13 | 2.12 | 2.12 | 2.12 | 2.11 | 2.11 |
| e | 2.12 | 2.12 | 2.12 | 2.10 | 2.12 | 2.11 |
| f | 1.43 | 1.44 | 1.43 | 1.45 | 1.44 | 1.43 |
| g | 1.37 | 1.37 | 1.38 | 1.35 | 1.35 | 1.38 |
| h | 1.40 | 1.39 | 1.39 | 1.41 | 1.41 | 1.40 |
| i | (1.22) | 1.30 | 1.36 | 1.36 | 1.34 | 1.36 |
| j | 1.46 | 1.42 | 1.42 | 1.42 | 1.42 | 1.43 |
| l | (1.18) | 1.29 | 1.35 | 1.34 | 1.34 | 1.35 |
| m | 1.42 | 1.40 | 1.41 | 1.40 | 1.38 | 1.38 |
| n | 1.38 | 1.39 | 1.37 | 1.36 | 1.37 | 1.37 |
| o | 1.41 | 1.42 | 1.43 | 1.43 | 1.42 | 1.44 |
| p | 1.46 | 1.45 | 1.46 | 1.44 | 1.44 | 1.44 |
| *Angles [°]* | | | | | | |
| *1* | *127* | *127* | *127* | *126* | *126* | *128* |
| *2* | *111* | *111* | *112* | *112* | *112* | *111* |
| *3* | *127* | *127* | *127* | *127* | *128* | *128* |
| *4* | *111* | *111* | *110* | *111* | *110* | *111* |
| *5* | *132* | *131* | *131* | *131* | *131* | *130* |
| *6* | *122* | *123* | *121* | *121* | *121* | *122* |
| *7* | *124* | *121* | *119* | *118* | *118* | *118* |
| *8* | *125* | *123* | *122* | *121* | *121* | *121* |
| α | *5* | *14* | *17* | *11* | 2 | *13* |
| Distances [Å] | | | | | | |
| a | 3.52 | 3.54 | 3.54 | 3.51 | 3.51 | 3.54 |
| b | 2.60 | 2.60 | 2.59 | 2.61 | 2.60 | 2.59 |
| c | 2.57 | 2.49 | 2.58 | 2.41 | 2.44 | 2.42 |

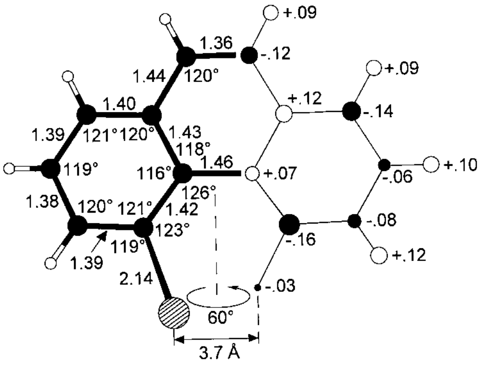
The positions of the six crystallographically independent 1,8-diiodonaphthalene molecules (Figure 3 C and Table 3) can be characterized as follows: The four denoted ③ to ⑥ are stacked in the $y$ direction, whereas the two marked ① and ② form layers perpendicular to the stacks, separating the latter from each other. Within the stacks, the molecules are packed alternately and the interplanar distances between their almost coplanar (idealized) molecular planes vary only slightly between 3.49 (0.006) and 3.52 (0.005) Å, that is, just 0.1 Å longer than the double van der Waals $\pi$ radius of 3.4 Å.[7a] Molecules of neighboring stacks exhibit a herringbone crystal-packing pattern with respect to each other, with an interplanar angle of 48° (Figure 3 A, C). The shortest intermolecular distance I–I determined amounts to 3.82 Å. All six independent molecules (Figure 3 C) show different structural parameters (Table 3). Of particular interest are the intramolecular distances between the iodine substituents, which range from only 3.51 (0.009) Å in molecule ⑤ (Figure 3 C) to 3.54 (0.008) Å in molecule ③ (Table 3), and concomitantly the torsion angles $\alpha$ of the $\pi$ systems, from 2° in molecule ⑤ to 17° in molecule ③ (Table 3). Based on the iodine van der Waals radius of 2.15 Å[7a] (Scheme 1), the distances I$\cdots$I between the iodine centers in 1,8-disubstituted naphthalene are shorter by about 0.78 Å or about 82 % within the van der Waals limit. The resulting I/I repulsion distorts the structure of the hydrocarbon skeleton significantly; in particular, the angles I-C1-C9 of 126 (0.6)° to 128 (0.7)° and C1-C9-C8 of 130 (0.7)° to 132 (0.7)° clearly reflect the interaction between the two iodine substituents. The central bond C9–C10 is stretched from 1.42 Å to 1.46(0.01) Å or the bonds C3–C4 and C5–C6 are compressed to rather short and partly even unrealistic distances between 1.29 (0.01) and 1.36 (0.01) Å (Table 3).

**Structural comparison based on density functional calculations**: The rather large distortions detected in some cases in the structure determination of the selected diiodo-substituted six-membered ring prototype hydrocarbons phenanthrene, biphenyl, and naphthalene, which predominantly involve torsion angles, but also bond angles and even bond lengths,[2, 5, 11, 14, 15] stimulated an extensive search for related molecules in the Cambridge Structural Database. The most relevant information extracted concerns the structure of 1,12-diiodotriphenylene, hidden in a short communication on the dilithiation of polycyclic aromatic hydrocarbons (Scheme 4).[16] On removal of the outer six-membered ring carbons C5 to C8, the molecule 1,10-diiodophenanthrene remains, for which a 5° smaller dihedral angle of 63° has been determined (Figure 1 and Table 1) together with an interiodine distance of 3.61 Å, 0.07 Å shorter than that of 1,12-diiodotriphenylene. These rather small structural differences may be rationalized by an increased stiffness of the triphenylene framework, but of more essential importance is the observed comparability for iodine/iodine interactions in the 2,2′-positions of rotationally restricted biphenyl skeletons.



Scheme 4. The structure of 1,12-diiodotriphenylene.

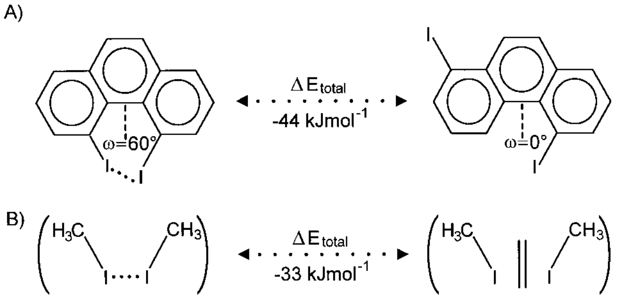
Full geometry optimization for the 24 atom/198 electron molecule 1,10-diiodophenanthrene with its total 66 degrees of freedom within a density functional B3LYP calculation using a 6-31G** basis set for carbon and hydrogen centers and additional 31G* effective pseudopotentials (ECP) for the iodine centers (Experimental Section) reproduces all essential details of the structure determined (Scheme 5, left-hand side).



Scheme 5. Left: Geometric parameters for 1,10-diiodophenanthrene from a density functional B3LYP calculation using a 6-31G** basis set for carbon and hydrogen centers and additional 31G* effective pseudopotentials (ECP) for the iodine centers; right: the Mulliken charge densities.

To begin with the I/I-enforced twisting (experimental values in brackets, Table 1), the rotational angle is calculated to be 60° (63°) and the distance I⋯I 3.7 Å (3.61 Å). The bonds C–I are calculated to be 2.14 Å (2.11 Å) long, and all the rather unused C–C bond lengths predicted are close to reality, from the long central C11–C12 bond of 1.46 Å (1.46 Å) to the shortest C5–C6 one of 1.35 Å (1.35 Å). Therefore, despite some hesitation, especially concerning the iodine centers, the Mulliken charge densities are also presented (Scheme 5, right-hand side). According to the DFT calculation, the iodine centers should be uncharged and the whole skeleton only negligibly polarized. The largest negative partial charges are predicted for the iodine-substituted carbon centers. The accumulation of partial positive charges on the peripheral hydrogens is a known artefactual phenomenon often observed for corrected C–H bond lengths.

To obtain energy estimates for both the repulsive I/I-interaction as well as for the loss of π-delocalization energy due to the enforced skeletal twisting, additional DFT model calculations were performed. The repulsion between the iodine centers at the 3.7 Å distance (Scheme 5) was approximated by considering a second 4,10-diiodo-substituted isomer, for which a difference in total energy $\Delta E(1{,}10-4{,}10) = 44\ \mathrm{kJ\,mol^{-1}}$ results (Scheme 6 A).



Scheme 6. A) Comparison of DFT total energies for 1,10- and 4,10-diiodo-substituted isomers; B) the I⋯I repulsion simulated by DFT model calculations for two methyl iodide subunits at the respective interiodine distances of the 1,10- and 4,10-diiodophenanthrene isomers.

In addition, the I⋯I repulsion was simulated by DFT model calculations for two methyl iodide subunits at the respective interiodine distances of the 1,10- and 4,10-diiodophenanthrene isomers (Scheme 6 B), for which a qualitative total energy difference of 33 kJ mol$^{-1}$ resulted (neglecting the basis set superposition error). Combining both DFT results in Scheme 6, the loss of π-delocalization energy due to the different twisting of the σ skeletons from $\omega = 0°$ to $\omega = 60°$ is estimated to be at least $\Delta\Delta E_{\mathrm{total}} \approx 10\ \mathrm{kJ\,mol^{-1}}$. This would correspond both to the value expected from simple π-perturbation arguments, $\beta = \beta_0(1-\cos^2\omega)$ with $(1-\cos^2(60°)) = 0.75$, a reduction of the π delocalization by only about 25%, as well as to the asymmetric energy hypersurface (Figure 4) calculated for the phenyl ring rotation around the

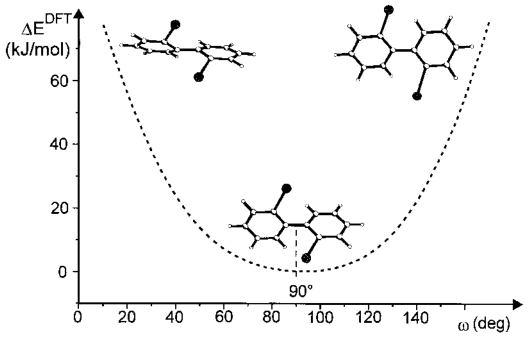


Figure 4. The asymmetric energy hypersurface for rotation around the central C–C bond in 2,2′-diiodobiphenyl.

central C–C bond in 2,2′-diiodobiphenyl, in which the stiffening (HC–CH) bridge of 1,10-diiodophenanthrene has been removed.

Starting from the twisted system with $\omega = 90°$, in which the π delocalization is by definition missing, an increase of $\Delta E^{\mathrm{DFT}}$ by about 10 kJ mol$^{-1}$ should turn the phenyl rings towards coplanarity by approximately 30°, close to the experimentally determined value $\omega = 63°$ (Figure 1 and Table 1). The comparison of the angle $\omega$ between 1,10-diiodophenanthrene and 2,2′-diiodobiphenyl can be further supported by comparable substituent effects depending on the van der Waals radii (Scheme 1) of one-center substituents. The slopes of the qualitative regression lines for both hydrocarbons (Figure 5) correspond approximately to changes $\Delta\omega$ of between 30° to 50° for a 0.8 Å increase in the van der Waals radii of the one-center substituents (Scheme 1).

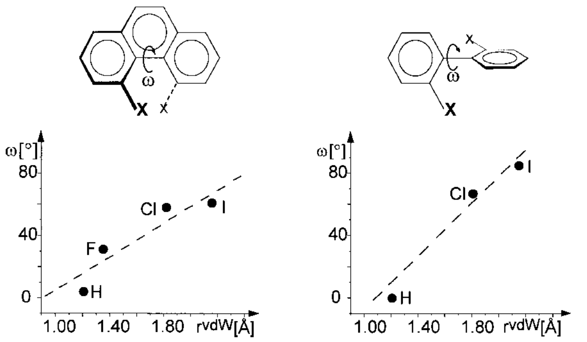
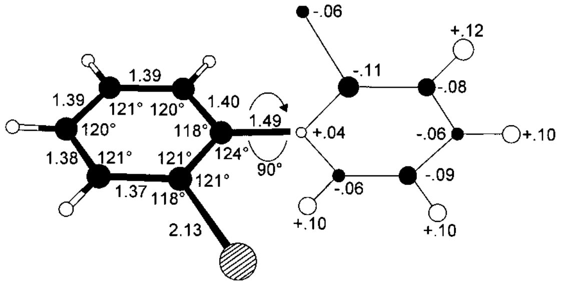


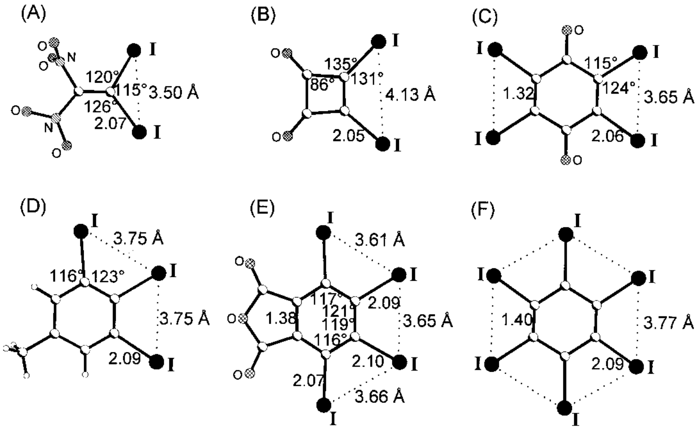
Figure 5. Effect of the substituent X on the angle $\omega$ in 1,10-diiodophenanthrene and 2,2′-diiodobiphenyl. The qualitative regression lines (- - -) for both hydrocarbons correspond approximately to changes $\Delta\omega$ of between 30° to 50° for a 0.8 Å increase in the van der Waals radii of the substituents.

As was the case for 1,10-diiodophenanthrene (Scheme 5), the geometry-optimized density functional calculations for 2,2′-diiodobiphenyl (Scheme 7, left-hand side) reproduce the experimentally determined structural parameters rather well (experimental values (Table 2) in brackets), from the 90° (85°) phenyl ring twisting through the 2.13 Å (2.11 Å) long C–I bonds to the 1.49 Å (1.50 Å) long central C–C bond. Comparable to those for 1,10-diiodophenanthrene (Scheme 5), the calculated Mulliken charge densities for 2,2′-diiodobiphenyl (Scheme 7, right-hand side) predict nearly uncharged iodine centers as well as a negligibly small polarization of the hydrocarbon skeleton, except for the artefactual $C^{\delta-}$–$H^{\delta+}$ bonds.



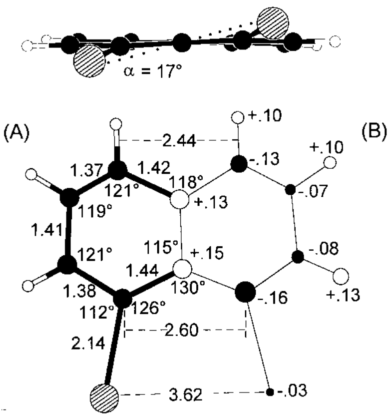
Scheme 7. Left: Geometric parameters for 2,2′-diiodobiphenyl from a density functional B3LYP calculation; right: the Mulliken charge densities.

An extensive CSD structure search for related polyiodine-substituted hydrocarbons revealed numerous derivatives with a planar skeleton analogous to prototype tetraiodoethylene (Scheme 1 B).[2] Selected examples are 1,1-diiododinitroethylene (Scheme 8 A),[17] 1,2-diiodocyclobutene-3,4-dione (Scheme 8 B),[18] 1,2,4,5-tetraiodo-*p*-benzoquinone (Scheme 8 C),[19] 3,4,5-triiodotoluolene (Scheme 8 D),[20] 2,3,4,5-tetraiodophthalic acid anhydride (Scheme 8 E),[21] and hexaiodobenzene (Scheme 8 F).[22] In 1,1-diiododinitroethylene, two electron-withdrawing nitro groups shorten the distance I⋯I between the geminal iodine centers of 3.50 Å relative to those in tetraiodoethylene of 3.54 Å (Scheme 18) by only 0.04 Å. Enlarging the angles C-C-I in 1,2-diiodocyclobutene-3,4-dione to 131° increases the distance I⋯I to 4.13 Å. In the 1,2,4,5-tetraiodo-*p*-benzoquinone with C=C bonds of 1.32 Å, the vicinal iodine centers are again 3.65 Å[21] apart as in $I_2C{=}CI_2$. Of the three benzene derivatives, both the fully planar hexaiodo derivative (F) as well as 1,2,3-triodotoluene show the obviously characteristic I⋯I distances of about 3.75 to 3.77 Å, whereas those in 2,3,4,5-tetraiodophthalic anhydride are reported to be shorter by about 0.2 Å;[21] recalculation from the structural data yields an average value of 3.64 Å. To summarize the iodine structural parameters in approximately planar polyiodosubstituted unsaturated hydrocarbons, typical bond lengths C–I are found within a rather narrow range between 2.05 and 2.10 Å, whereas the intermolecular I⋯I distances between adjacent iodine centers range from 3.50 to 3.77 Å depending on the skeletal topology (Scheme 8).



Scheme 8. Planar polyiodine-substituted hydrocarbons (cross-hatched circles: O; shaded circles: N; empty circles: C).

It was this overview that tempted us to prepare 1,8-diiodonaphthalene again[13] and to determine its structure, because the distance between its 1,8-peri positions amounts to only about 2.42 Å and, therefore, only about 56 % of the double iodine van der Waals radius $2r_{\mathrm{I}}^{\mathrm{vdW}} = 4.30$ Å. A CSD search reveals the structures of numerous crystalline 1,8-naphthalene derivatives, for instance with substituents X = F,[23] Cl,[24] Br,[25] or even Si(CH$_3$)$_3$,[26] but no iodine-substituted one. The structure determined for 1,8-diiodonaphthalene and described earlier (Figure 3 and Table 3) exhibits unusual facets: There are six independent molecules with distances I ··· I between 3.51 to 3.54 Å and torsion angles $\alpha$ (I-CCC-I) between 2 and 17°, indicating dynamic flexibility of the hydrocarbon with rather low activation barriers. Again the density functional calculations (cf. Schemes 5 and 7) reflect the experimental observations. To begin with, the difference in DFT total energy between conformers twisted by $\alpha = 10°$ and 17° (Figure 3E) amounts to only 0.6 kJ mol$^{-1}$ (!). For the one with the maximum twist angle, $\alpha = 17°$, the geometry-optimized parameters (Scheme 9, left-hand side) are calculated, closely reproducing the experimentally determined ones (Table 3). The molecular skeleton of 1,8-diiodonaphthalene is heavily distorted (experimental values (Table 3) in brackets); the distance I ··· I of 3.62 Å (3.54 Å) creates the C1 ··· C8 one of 2.60 Å (2.59 Å) in the C1-C9-C8 subunit, which has C–C bond lengths of 1.43 Å (1.44 Å) and an angle of 130° (131°). The central C–C ring connection of 1.45 Å (1.46 Å) is close to the length of an ordinary single bond and only the opposite angle $\sphericalangle$C-C-C of 118° (Table 3/angle 7: 119°) returns to a normal value. The accompanying Mulliken charge densities (Scheme 9, right-hand side) indicate neutral iodine centers again (cf. Schemes 5 and 7), but a considerable polarization of the inner C–C bond versus the peripheral ones suggests that a radical anion of 1,8-diiodonaphthalene might be accessible by reduction or that the neutral molecule possibly exerts special π-acceptor properties towards electron-rich small donors.



Scheme 9. Left: Geometric parameters for the 1,8-diiodonaphthalene skeleton with the maximum twist, $\alpha = 17°$, from a density functional B3LYP calculation; right: the Mulliken charge densities.

Most intriguing of all DFT results, however, may be the small total energy differences already pointed out, which do to explain the existence of the six independent molecules found in the triclinic crystal of 1,8-diiodonaphthalene (Figure 3C) and provide snapshot impressions of its molecular dynamics.

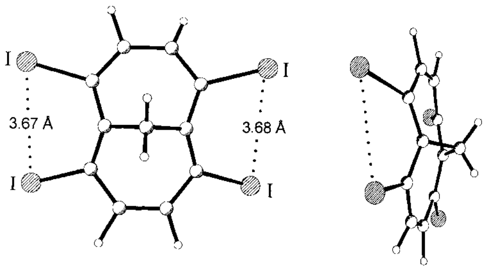
## Conclusions and Perspectives

Three diiodosubstituted hydrocarbon derivatives were selected to study the repulsive interactions between adjacent iodine centers and the accompanying skeletal distortions. The largest interiodine distance of 4.35 Å in the rather flexible 2,2′-biphenyl, with the density functional calculated minimum at a 90° rotational angle, is shortened to 3.61 Å in 1,10-diiodophenanthrene by a stiffening phenylene bridge. Estimates for the I ··· I repulsion and for the π-delocalization loss due to the skeletal twisting by a 63° dihedral angle suggest minimum energy contributions of about 30 kJ mol$^{-1}$ and 10 kJ mol$^{-1}$. If planarity is either present, as in the prototype derivatives tetraiodoethylene and hexaiodobenzene, or enforced, as in 1,8-diodonaphthalene, other distortions involving bond angles or even bond lengths may be observed depending on the topology of the π system.

For rationalization of the structural distortions, arguments based on the (average) van der Waals radius of iodine, $r_{\mathrm{I}}^{\mathrm{vdW}} = 2.15$ Å, are often quite helpful, if their limited directionality and their considerable compressibility are kept in mind. Most valuable information is provided by (approximate) density functional calculations, for which the iodine basis set could be improved to reproduce most of the structural parameters experimentally determined. Accompanying Mulliken charge densities suggest only negligible polarization in the iodine-substituted hydrocarbons close to the iodine centers.

Iodine compounds are fascinating—from novel triatomic molecules such as $SiI_2$ generated under unimolecular conditions in the gas phase 5 years ago [Eq. (1)], for which calculations using a highly correlated relativistic pseudopotential wavefunction were carried out[27] to all the interesting novel organic compounds published day by day, such as 2,5,7,10-tetraiodo-1,6-methano[10]annulene (Scheme 10).[28]

$$SiI_4 + [Si]_x \rightarrow 2\,SiI_2 \qquad (1)$$



Scheme 10. 2,5,7,10-Tetraiodo-1,6-methano[10]annulene.

The rather bulky iodine centers in appropriate molecules should be more extensively explored, because of their potential shielding of reactive centers and, above all, because they can act as both σ donors and π acceptors.[29–31]

## Experimental Section

**1,10-Diiodophenanthrene**:[9] Phenanthrene (10.65 g, 60 mmol) was suspended under argon in tetramethylethylenediamine (17.7 mL) and, after cooling with ice, a solution of *n*-butyllithium in *n*-hexane (1.6 M, 75 mL) added under constant stirring. The resulting dark brown mixture was heated under reflux to 70 °C for 3 h to evaporate the butane gas. After standing for 24 h at room temperature, the black mixture was cooled with ice again and the crude dilithium phenanthrene filtered off under argon.[10]

Its solution in THF (90 mL) was cooled to $-75\,^{\circ}C$; iodine (9.8 g, 38.5 mmol) was added, and the mixture stirred at room temperature for 17 h. After quenching with water added dropwise (20 mL) the solution was extracted twice with ether (each 50 mL); the combined ether phases were washed first with 40% $NaHSO_3$ solution and then four times with water (each 50 mL). The ether solution dried over $MgSO_4$ and evaporated yields 1,10-diiodophenanthrene as a light brown product, which can be recrystallized at $-20\,^{\circ}C$ after addition of *n*-hexane (m.p. 188–193 °C).

**Crystal structure determination for 1,10-diiodophenanthrene**: 1,10-Diiodophenanthrene, brown blocks, $C_{14}H_8I_2$ ($M_r = 430$), $a = 877.2(1)$, $b = 877.4(1)$, $c = 1658.2(1)$ pm, $\alpha = 105.03(1)^{\circ}$, $\beta = 100.28(1)^{\circ}$, $\gamma = 90.15(1)^{\circ}$, $V = 1211.2 \times 10^6$ pm$^3$ ($T = 150$ K), $\rho_{ber} = 2.358$ g cm$^{-3}$, triclinic, $P\bar{1}$ (No. 2), $Z = 4$, $F(000) = 792.0$, $\omega - \theta$ scan on a Siemens P4 four-circle diffractometer, $Mo_{K\alpha}$ radiation, $\mu = 5.16$ mm$^{-1}$, all data corrected for Lorentz and polarization effects and absorption correction established by DIFABS.[32] Range $3 \leq 2\theta \leq 66^{\circ}$; 9728 reflections, of which 8936 independent and 8185 used for refinement ($R_{int} = 0.0211$). Structure solution with direct methods by means of SHELXS-86, refinement with SHELXL-93, 290 parameters, $w = 1/[\sigma 2(F_o^2) + (0.0298P)^2 + 2.49P]$, $R = 0.0401$ for 8185 $F_o > 4\sigma(F_o)$, $wR2 = 0.0979$ for all 9728 reflections, GoF = 1.231, residual density: 1.45/−1.20 e Å$^{-3}$. All heavy centers were refined with anisotropic displacement parameters and all hydrogens located from the difference map, positioned ideally, and refined with isotropic displacement parameters using the riding model ($[U_{iso} = 1.2\,U_{eq}(C-H/CH_2)]$; $[U_{iso} = 1.5\,U_{eq}(C-H/CH_3)]$).

**2,2′-Diiodobiphenyl**:[10] Biphenyl (4.7 g, 30.5 mmol) was stirred under argon in *n*-butyllithium in *n*-hexane solution (1.6 M, 46 mL, 74 mmol) and then heated to 60 °C for 3 h. After standing at room temperature for 10 h, the mixture was cooled to $-20\,^{\circ}C$, the resulting light yellow solid filtered off, pure THF (20 mL) added and the red solution cooled to $-75\,^{\circ}C$. Under argon, iodine (15 g, 59 mmol) was added, and the dark brown solution allowed to warm up to room temperature and stirred for 2 h. On shaking the mixture with ether and 40% $NaHSO_3$ solution, it turned orange. Washing with water to neutral pH and evaporation yielded a dark oil, from which on addition of *n*-hexane a light yellow solid precipitated. Crystals of 2,2′-diiodobiphenyl are best obtained by a 7-day sublimation at 70 °C and 10 mbar (m.p. 109 °C).

**Crystal structure determination for 2,2′-diiodobiphenyl**: 2,2′-Diiodobiphenyl, yellow rods, $C_{12}H_8I_2$ ($M_r = 405.98$), $a = 767.4(1)$, $b = 1412.7(2)$, $c = 2212.4(2)$ pm, $\alpha = \beta = \gamma = 90^{\circ}$, $V = 2398.5 \times 10^6$ pm$^3$ ($T = 200$ K), $\rho_{ber} = 2.249$ g cm$^{-3}$, orthorhombic, *P*bca (No. 61), $Z = 8$, $F(000) = 1488.0$, $\omega - \theta$ scan on a Siemens/Stoe AEDII four-circle diffractometer, $Mo_{K\alpha}$ radiation, $\mu = 5.21$ mm$^{-1}$, all data corrected for Lorentz and polarization effects and empirical absorption correction established by XEMP (min. transm. = 0.730, max transm. = 0.993).[33] Range $3 \leq 2\theta \leq 52^{\circ}$; 3215 reflections, of which 2322 independent and 1755 used for refinement ($R_{int} = 0.0117$). Structure solution with direct methods using SHELXS-86, refinement with SHELXL-93, 128 parameters, $w = 1/[\sigma^2(F_o^2) + (0.0259P)^2 + 3.27P]$, $R = 0.0246$ for 1755 $F_o > 4\sigma(F_o)$, $wR2 = 0.0645$ for all 3215 reflections, GoF = 1.042, residual density: 0.90/−0.65 e Å$^{-3}$. All centers were refined with anisotropic displacement parameters and all hydrogens located from the difference map, positioned ideally, and refined with isotropic displacement parameters using the riding model ($[U_{iso} = 1.2\,U_{eq}(C-H/CH_2)]$; $[U_{iso} = 1.5\,U_{eq}(C-H/CH_3)]$).

**1,8-Diiodonaphthalene**:[13] The compound is prepared in two steps via 1,8-iodonaphthylamine hydrochloride (see Scheme 3).

*1,8-Iodonaphthylamine hydrochloride*: A hot solution of 1,8-naphthylendiamine (15 g, 95 mmol) in conc. HCl (200 mL) was poured into water (1400 mL); the solution was filtered and cooled by adding ice (300 g). Subsequently, $H_2SO_4$ (15 mL) and $NaNO_2$ (6.7 g, 97 mmol) were added under constant stirring and after cooling the temperature to well below 5 °C. The product was filtered off, dried at $10^{-2}$ mbar and suspended in HI (100 g, 781 mmol). Under constant stirring, copper metal (4 g, 63 mmol) was added in small portions and the reaction mixture heated for 2 h on a waterbath. Under vigorous liberation of nitrogen, a black crystalline product formed, which could be recrystallized from hot ethanol to yield grey needles of 1,8-iodonaphthylamine hydrochloride. This was purified by refluxing with diethyl ether for 2 h, drying the filtered solution with $K_2CO_3$ and precipitating the hydrochloride salt with aqueous HCl. Recrystallization from hot ethanol yielded light gray needles (m.p. 186–189 °C).

*1,8-Diiodonaphthalene*: 1,8-Iodonaphthylamine hydrochloride (6.3 g, 24 mmol) was dissolved in conc. HCl (71 mL) and cooled to $-1\,^{\circ}C$; under stirring $NaNO_2$ (1.46 g, 21 mmol) was added in small portions. On addition of KI (5.5 g, 33 mmol), the yellow-brown solution of the diazonium chloride turned into the red one of diazonium iodide. After heating the mixture for 2 h on a waterbath, nitrogen evolution ceased; the crude product was recrystallized from methanol to yield orange-brown needles (m.p. 109 °C).

**Crystal structure determination for 1,8-diiodonaphthalene:** 1,8-Diiodonaphthalene, orange-brown needles, $C_{10}H_6I_2$ ($M_r = 379.95$), $a = 1283.8(2)$, $b = 1540.2(2)$, $c = 1599.9(2)$ pm, $\alpha = 77.16(1)$, $\beta = 72.64(1)$, $\gamma = 82.26(1)^{\circ}$, $V = 2935.9 \times 10^6$ pm$^3$ ($T = 200$ K), $\rho_{ber} = 2.579$ g cm$^{-3}$, triclinic, $P\bar{1}$ (No. 2), $Z = 12$, $F(000) = 2064.0$. $\omega - \theta$ scan on a four-circle diffractometer Siemens/Stoe AEDII, $Mo_{K\alpha}$ radiation, $\mu = 6.37$ mm$^{-1}$, all data corrected for Lorentz and polarization effects and absorption correction established by PSI-scan measuring 10 reflections in steps of 10°. In the range $3 \leq 2\theta \leq 52^{\circ}$ are measured 9962 reflections, of which 9251 independent and 7766 used for refinement ($R_{int} = 0.0863$). Structure solution with direct methods using SHELXS-86, refinement with SHELXL-93, 650 parameters, $w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 20.76P]$, $R = 0.0408$ for 7766 $F_o > 4\sigma(F_o)$, $wR2 = 0.1152$ for all 9962 reflections, GoF = 1.057, residual density: 3.33/−2.14 e Å$^{-3}$. All heavy centers were refined by means of anisotropic displacement parameters and all hydrogens located from the difference map, positioned ideally, and refined with isotropic displacement parameters using the riding model ($[U_{iso} = 1.2\,U_{eq}(C-H/CH_2)]$; $[U_{iso} = 1.5\,U_{eq}(C-H/CH_3)]$).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101284. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

**Density functional calculations** are performed at the B3LYP level[34–36] with 631G** basis sets[37–39] for centers H and C. For iodine, the effective core potential known from the literature[40] was modified to extend the valence basis set to (4s,4p). The uncontracted gaussians were simultaneously optimized for the I atom (at the B3LYP level), the polarization *d* function ($\alpha = 0.246$, optimized for HI) added and the valence basis set contracted to double-zeta 31G* quality. The resulting basis set for iodine fits the 6-31G** basis set of the other atoms. All molecules studied were totally geometry-optimized. To compute the rotational potential energy surface of 1,1′-diiodobiphenyl, the central (H)C-C-C-C(H) torsion angle was varied in 10° steps and all the other parameters optimized.

**Acknowledgements**: Our investigations have been generously supported by the Deutsche Forschungsgemeinschaft, the State of Hesse, the Hoechst Corporation and the Fonds der Chemischen Industrie.

Received: August 20, 1997 [F798]

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