The structure of the molecule is a "cisoid form" as is shown in Scheme I, which is very rare among diolefinic molecules having photoreactivity in the crystalline state; a "transoid form" has been confirmed in many cases by X-ray crystal structure analysis. Every pair of reactive molecules having a quasi-C_2 symmetry is arranged according to β-type packing.[7] No stack for the formation of a high molecular weight polymer exists; the dimer is thus formed as a major product when only the monomer is excited. The intermolecular distances of two facing double bonds are approximately within the normal photoreactive distance (3.802 and 4.387 Å for one pair of facing double bonds, and 3.829 and 4.123 Å for another). Due to the different distances and nonparallelisms, the two pairs of reacting double bonds are expected to differ from one another in reactivity. It is apparent, however, that a dimer having the same chirality is formed by a reaction of either of the two pairs of double bonds. On the other hand, in the β-type packing crystal of "transoid" molecules, two reacting molecules are related by centrosymmetry, and therefore the four carbons on a cyclobutane ring derived from reacting pairs of double bonds should have opposite chiralities resulting in the racemic dimer.[8]

In contrast to asymmetric synthesis using α-type packing chiral crystals as reported by Addadi et al.,[2a] this result is the first demonstration of asymmetric synthesis in a β-type packing crystal. The formation of a chiral space group in a β-type packing crystal is caused by the "cisoid form" of the molecular structure of 2. The present results contribute to the further development of photoreactive chiral crystals for asymmetric synthesis.

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Supplementary Material Available: Atomic coordinates and thermal parameters for 1 (2 pages). Ordering information is given on any current masthead page.

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(6) Crystal data: MW = 279, orthorhombic, $P2_12_12_1$, $a = 19.442$ (5) Å, $b = 15.112$ (4) Å, $c = 10.192$ (3) Å, $V = 2994.6$ Å^3, $Z = 8$, $R = 0.068$ ($R_w = 0.076$).

(7) The arrangement of diolefinic molecules in photoreactive organic crystals may be conveniently divided into two groups: α-type packing, in which molecules are stacked with displacement along the molecular axis by half a molecule, and β-type packing, in which molecules are stacked with overlap.

(8) Kato, S.; Nakatani, M.; Harashina, H.; Saigo, K.; Hasegawa, M.; Sato, S. *Chem. Lett.* **1986**, 847–850.

Synthesis of Chiral Hypervalent Organoiodinanes, Iodo(III)binaphthyls, and Evidence for Pseudorotation on Iodine

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Hypervalent organoiodinanes are versatile reagents in organic synthesis and continue to find many applications for the preparation of a variety of functional groups.[1] Asymmetric oxidation of sulfides to sulfoxides by utilizing organoiodinanes generated

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(1) For reviews, see: (a) Banks, D. F. *Chem. Rev.* **1966**, *66*, 243. (b) Koser, G. F. *The Chemistry of Functional Groups, Supplement D*; Wiley: New York, 1983; Chapter 18. (c) Varvoglis, A. *Synthesis* **1984**, 709. (d) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. (e) Merkushev, E. B. *Russ. Chem. Rev. (Engl. Transl.)* **1987**, *56*, 826. (f) Ochiai, M. *Rev. Heteroatom Chem.* **1989**, *2*, 92.
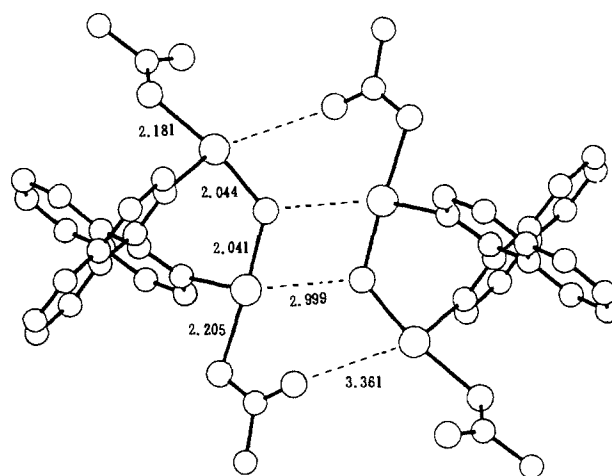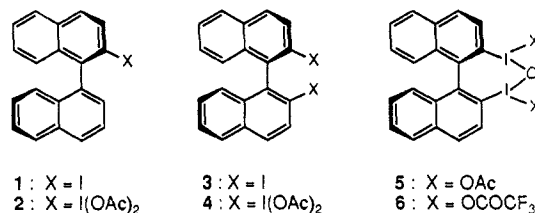
Figure 1. Molecular arrangement around an inversion center, showing a bimolecular unit formed in the crystal of the inclusion compound of racemic 5 and benzene, and critical bond length (Å).[11]

in situ from iodosylbenzene and L-tartaric anhydrides has been reported.[2,3] We report herein the first example of synthesis of hypervalent organoiodinanes bearing chiral carbon ligands, acetoxyiodo(III)binaphthyls, and their degenerate isomerization of acetoxy ligands about iodine.

Diazotization of optically active (*S*)-2-amino-1,1′-binaphthyl[4] with $NaNO_2$ in H_2SO_4 and then $KI-ZnI_2$, followed by decomposition of the resulting diazonium salt, afforded (*S*)-2-iodo-1,1′-binaphthyl (1). Treatment of the corresponding (dichloroiodo)binaphthyl, prepared from 1 by chlorination in dry hexane,[6] with mercuric acetate in carbon tetrachloride gave the desired (*S*)-2-(diacetoxyiodo)-1,1′-binaphthyl (2) ($[\alpha]^{18}_D$ +51.9° (*c* 0.97, $CHCl_3$)) in 83% yield.[7] More conveniently, (*S*)-2 could be prepared quantitatively by sodium perborate oxidation of 1 in acetic acid.[8] Oxidation of the known (*R*)-diiodide 3, previously prepared by Murdoch and his co-workers,[5] with sodium perborate gave an 85% yield of the C_2 chiral tetraacetate (*R*)-4 ($[\alpha]^{21}_D$ −35.7° (*c* 0.90, AcOH)), which gradually decomposed to the cyclic μ-oxo-diiodinane (*R*)-5 ($[\alpha]^{19}_D$ +254.4° (*c* 0.75, $CHCl_3$)) in chloroform solution at room temperature. The reaction is reversible, and exposure of 5 to warm acetic acid gave 4. Chlorination of (*R*)-3 and then ligand exchange using mercuric bis(trifluoroacetate) afforded the μ-oxo-bis(trifluoroacetate) (*R*)-6 ($[\alpha]^{17}_D$ +185.0° (*c* 0.98, $CHCl_3$)) (75% yield).

1 : X = I
2 : X = I(OAc)$_2$

3 : X = I
4 : X = I(OAc)$_2$

5 : X = OAc
6 : X = OCOCF$_3$

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(2) Imamoto, T.; Koto, H. *Chem. Lett.* **1986**, 967.

(3) For organoiodinanes bearing chiral oxygen ligands, see: (a) Hatzigrigoriou, E.; Varvoglis, A.; Bakola-Christianopoulou, M. *J. Org. Chem.* **1990**, *55*, 315. (b) Merkushev, E. B.; Novikov, A. N.; Makarchenko, S. S.; Moskalchuk, A. S.; Glushkova, V. V.; Kogai, T. I.; Polyakova, L. G.; *Zh. Org. Khim.* **1975**, *11*, 1259.

(4) (*S*)-2-Amino-1,1′-binaphthyl ($[\alpha]^{20}_D$ +87.7° (*c* 1.08, THF)) was prepared from (*R*)-2,2′-diamino-1,1′-binaphthyl:[5b] (a) Akimoto, H.; Yamada, S. *Tetrahedron* **1971**, *27*, 5999. (b) Kabuto, K.; Yasuhara, F.; Yamaguchi, S. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1263. (c) Tomoda, S.; Iwaoka, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1283.
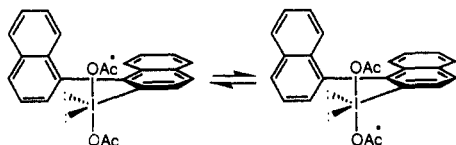
(5) (a) Brown, K. J.; Berry, M. S.; Waterman, K. C.; Lingenfelter, D.; Murdoch, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 4717. (b) Brown, K. J.; Berry, M. S.; Murdoch, J. R. *J. Org. Chem.* **1985**, *50*, 4345.

(6) (a) Willgerodt, C. *J. Prakt. Chem.* **1886**, *33*, 155. (b) Lucas, H. J.; Kennedy, E. R. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 482.

(7) Taylor, R. T.; Stevenson, T. A. *Tetrahedron Lett.* **1988**, *29*, 2033.

(8) McKillop, A.; Kemp, D. *Tetrahedron* **1989**, *45*, 3299.

Scheme I

The optical purity of these chiral binaphthyls **2** and **4–6** was determined from the ^{1}H NMR spectra of the corresponding α-methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA) derivatives, which were prepared by ligand-exchange reaction with (*R*)-MTPA.[9] Reaction of (*S*)-**2** with 2.1 equiv of (*R*)-MTPA in chlorobenzene under reduced pressure quantitatively afforded 2-(bis(2-methoxy-(2-trifluoromethyl)phenylacetoxy)iodo)-1,1'-binaphthyl (≥97% ee). The high optical purity of the other iodinanes (≥97% ee) was determined similarly. Figure 1 shows the crystal structure of the 1:1 inclusion compound of racemic μ-oxo-diacetate **5** and benzene, which is a dimer consisting of a pair of (*R*)- and (*S*)-**5**.[10,11] There are two primary hypervalent I–O bonds on each iodine atom of T-shaped geometry with considerably ionic exocyclic bonds to the acetate oxygen and strong endocyclic bonds to ring oxygen.[12,13] Most importantly, these bonds overlap well with the two aromatic rings, which are almost perpendicular, with an angle of 81.1 (2)°.

Little is known about the configurational stability of organoiodinanes. Degenerate ligand exchange of cyclic dialkoxyiodinanes, stabilized by the five-membered-ring effect, has been reported to occur via an associative mechanism;[14] however, the pseudorotation pathway for the interchange of ligand positions about iodine has not been observed.[15]

The establishment of a synthetic method for (diacetoxyiodo)-binaphthyls has shed light on the configurational stability of organoiodinanes. The ^{1}H NMR spectra of **2** show dynamic behavior. The two acetoxy groups are anisochronous in CDCl$_3$ at −10 °C and appear at δ 1.52 and 2.0 ppm as sharp singlets. The observed high shielding of one of the acetoxy groups is attributed to the stereochemical arrangement of **2** shown in Scheme I, which is consistent with the results of the X-ray structure analysis of

5.[16] These two singlets coalesce at 34 °C to one singlet at 1.73 ppm with a free activation energy of 15.1 kcal/mol. Similar temperature dependence was observed in the ^{13}C NMR spectrum: the low-temperature spectrum in CDCl$_3$ (−20 °C) has methyl carbon signals at δ 20.7 and 19.9 ppm and carbonyl carbon signals at δ 176.5 and 176.2 ppm. The carbonyl signals coalesce to δ 176.3 ppm at 10 °C and the methyl signals to δ 20.0 ppm at 21 °C.[17] All line-shape changes are reversible. These results, combined with no temperature dependence of binaphthylyl aromatic resonances both in ^{1}H and ^{13}C NMR spectra and also no loss in optical purity of (*S*)-**2** during dynamic NMR measurements, can be rationalized in terms of the degenerate isomerization of the acetoxy groups of **2** between two apical sites in keeping with the equatorial binaphthylyl group (Scheme I).

We propose that the degenerate isomerization of **2** is caused by rapid pseudorotation pathways on iodine. The isomerization process via the rotation about the binaphthylyl–iodine(III) bond can be ruled out by the following observation. The rotation mechanism about the σ-bond would result in a higher isomerization barrier for the tetraacetate (**4**) than **2**, because of severe steric crowding in the transition state for the isomerization of **4**. However, the isomerization rate of **4** is about twice that of **2**, and the two acetoxy singlets of **4** at −25 °C (^{1}H NMR (CDCl$_3$): δ 2.06 and 1.12) coalesce at 3 °C with $\Delta G^* = 13.2$ kcal/mol.[19]

Bimolecular ligand exchange is not compatible with the fact that the dynamic ^{1}H NMR spectrum is independent of the concentration of **2** in the range 0.065–0.5 M. The degenerate isomerization is not catalyzed by acids and bases: addition of AcOH and pyridine does not lead to any change of the coalescence temperature ($T_c = 34$ °C). Since the methyl resonance of the added AcOH appears as a very sharp singlet at the coalescence temperature, intermolecular ligand exchange with AcOH is negligibly small on the NMR time scale. Most importantly, the possibility that **2** is dimeric in solution and the dimerization is the mechanism of exchange of acetoxy ligands[20] does not agree with the observation that the dynamic behavior of racemic and of optically active **2** in ^{1}H NMR spectra are identical.[21]

Thus the degenerate isomerization of **2** can be interpreted in terms of a unimolecular isomerization mechanism. This is the first observation suggesting that, in spite of the presence of two lone pairs on iodine(III), pseudorotation of diacetoxyiodinanes probably takes place.

Supplementary Material Available: Tables of crystallographic details, atomic coordinates and isotropic temperature factors, anisotropic thermal parameters, and bond lengths and angles and the molecular structure of **5** and dynamic ^{1}H and ^{13}C NMR spectra of **2** (9 pages). Ordering information is given on any current masthead page.

(9) (a) Pausacker, K. H. *J. Chem. Soc.* **1953**, 107. (b) Merkushev, E. B.; Novikov, A. N.; Makarchenko, S. S.; Moskal'chuk, A. S.; Glushkova, V. V.; Kogai, T. I.; Polyakova, L. G. *J. Org. Chem. USSR (Engl. Transl.)* **1975**, 1246. (c) Stang, P. J.; Boehshar, M.; Wingert, H.; Kitamura, T. *J. Am. Chem. Soc.* **1988**, *110*, 3272.

(10) Since no significant interaction was observed between **5** and benzene in the crystal structure of the complex, obtained by recrystallization from benzene–petroleum ether, Figure 1 shows only racemic **5**.

(11) For the crystal structure of acyclic μ-oxo-diiodinanes, see: (a) Alcock, N. W.; Countryman, R. M. *J. Chem. Soc., Dalton Trans.* **1979**, 851. (b) Gallos, J.; Varvoglis, A.; Alcock, N. W. *J. Chem. Soc., Perkin Trans. 1* **1985**, 757.

(12) The endocyclic I–O distances are almost comparable to the computed covalent single bond length of 1.99 Å: Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, 1960; Chapter 7.

(13) The lower carbonyl frequencies of **5** (1600 cm^{-1}) in the IR spectrum compared to those of (diacetoxyiodo)benzene (1640 cm^{-1}) are attributed to the greater degree of polarity in the I–OAc bond in **5**: Bell, R.; Morgan, K. J. *J. Chem. Soc.* **1960**, 1209.

(14) (a) Amey, R. L.; Martin, J. C. *J. Org. Chem.* **1979**, *44*, 1779. (b) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 902. (c) Nguyen, T. T.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3803.

(15) Degenerate isomerization of cyclic triaryliodinanes has been reported: Reich, H. J.; Cooperman, C. S. *J. Am. Chem. Soc.* **1973**, *95*, 5077.

(16) Methyl protons of **5** appear at δ 1.79 ppm as a singlet.

(17) It has been shown that activation entropies determined by dynamic NMR are not reliable,[18] but these results lead to $\Delta H^* = 11.5$ kcal/mol and $\Delta S^* = -5.9$ eu.

(18) Binsch, G. *Top. Stereochem.* **1968**, *3*, 97.

(19) The rapid rate of isomerization for **4** is likely to be due to the considerable steric acceleration.

(20) Fluorine exchange of ClF$_3$ has been proposed to occur through a dimer intermediate: Muetterties, E. L.; Phillips, W. D. *J. Am. Chem. Soc.* **1957**, *79*, 322.

(21) By analogy to the crystal structure of **5**, the *R,S* dimer of C_i symmetry in racemic **2** is expected to be the most stable.