# Spontaneous Generation of Chirality in Simple Diaryl Ethers

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*ABSTRACT* We studied the spontaneous formation of chiral crystals of four diaryl ethers, 3-phenoxybenzaldehyde, 1; 1,3-dimethyl-2-phenoxybenzene, 2; di(4-aminophenyl) ether, 3; and di(*p*-tolyl) ether, 4. Compounds 1, 3, and 4 form conformationally chiral molecules in the solid state, while the chirality of 2 arises from the formation of supramolecular helices. Compound 1 is a liquid at ambient temperature, but 2–4 are crystalline, and solid-state CD-spectroscopy showed that they could be obtained as optically active bulk samples. It should be noted that the optical activity arise upon crystallization, and no optically active precursors were used. Indeed, even commercial samples of 3 and 4 were found to be optically active, giving evidence for the ease at which total spontaneous resolution may occur in certain systems. *Chirality* 27:425-429, 2015. © 2015 Wiley Periodicals, Inc.

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The optical activity displayed by drugs, catalysts, and other important chemicals can always be traced back to the so-called chiral pool, i.e., naturally occurring optically active substances like L-amino acids, D-sugars, alkaloids, etc.<sup>1</sup> The origin of this biomolecular homochirality is unknown.<sup>2,3</sup> A strategy in the search for clues to this important question is to study processes capable of transforming racemic or achiral starting materials to optically active products without chiral reagents or catalysts; such processes are generally termed absolute asymmetric synthesis.<sup>4-6</sup> Different strategies for achieving absolute asymmetric synthesis include reactions under the influence of circularly polarized light,<sup>4</sup> abrasion/grinding techniques,<sup>7,8</sup> and total spontaneous resolution.<sup>9</sup> The latter is the subject of this article. When a chiral compound crystallizes in one of the so-called Sohncke<sup>10</sup> (or chirodescriptive)<sup>11</sup> space groups, it will crystallize as a 1:1 mixture (a conglomerate) of enantiomerically pure crystals. Such a substance is said to undergo spontaneous resolution, since the two enantiomers will crystallize separately. Spontaneous resolution was first observed in ammonium sodium tartrate by Louis Pasteur.<sup>12</sup> On crystallization of a stereochemically labile substance one does not necessarily obtain a 1:1 mixture of the two enantiomorphs. If crystallization is initiated by a single nucleus, total spontaneous resolution (crystallization-induced asymmetric transformation) is possible, meaning that a majority of the crystals will be clones of this original nucleus and hence be of the same enantiomorph. The bulk will then be obtained in an optically active state, and total spontaneous resolution means that an excess (but not necessarily 100%) is obtained of one enantiomorph. Over the past years, we have studied total spontaneous resolution and absolute asymmetric synthesis of a variety of molecules, ranging from pure organic substances<sup>13</sup> to organometallic reagents<sup>14–19</sup> and coordination compounds.<sup>20–23</sup> In this work we study four simple diaryl ethers, 3-phenoxybenzaldehyde, 1; 1,3-dimethyl-2phenoxybenzene, 2; di(4-diaminophenyl) ether, 3; and di (p-tolyl) ether, 4 (Scheme 1), all of which spontaneously form chiral crystals.

## MATERIALS AND METHODS

Commercial 3-phenoxybenzaldehyde (Aldrich, Milwaukee, WI) was dissolved in hexane/dichloromethane 1:1. Cooling to  $-35^{\circ}$ C afforded colorless crystals of **1** suitable for single-crystal X-ray diffraction and solid-state CD-spectroscopy. Commercial di(4-aminophenyl) ether (Aldrich) was recrystallized from boiling methanol to give crystals of **3**. Crystals of **4** were obtained by dissolving commercial di(*p*-tolyl)ether (Aldrich) in 96% ethanol and cooling the solution to  $-20^{\circ}$ C. Solid-state CD-spectra were recorded in KBr-discs (1 mg sample, 100 mg KBr, 8 tons pressure) on a Jasco (Tokyo, Japan) J-175 spectropolarimeter.

## 1,3-Dimethyl-2-Phenoxybenzene, 2

2,6-dimethylphenol (10.4 g, 0.085 mol) and potassium hydroxide (4.3 g, 0.072 mol) were fused, and copper(I) chloride (0.22 g) and bromobenzene (5.0 mL, 0.050 mol) were added. The mixture was heated under reflux for 8 h and poured into a 2 M solution of sodium hydroxide in icewater (100 mL). The mixture was extracted with diethyl ether (3 × 50 mL). The red solution was washed with 2 M aqueous sodium hydroxide (100 mL) and with small portions of water, until no colored material was extracted. The ethereal solution was washed with brine (50 mL), dried over sodium sulfate, and evaporated in vacuo. The residue was recrystallized from hot ethanol, which afforded colorless crystals of **2**. Yield: 1.4 g (14%). Analytical data were consistent with previously published data.<sup>24</sup>

#### Crystal Structure Determination

Crystals were selected using a microscope and transferred to a Rigaku R-AXIS IIc image plate system. Diffracted intensities were measured using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) from a RU-H3R rotating anode operated at 50 kV and 90 mA. Ninety oscillation photographs with a rotation angle of 2° were collected and processed using the CrystalClear software package.<sup>25</sup> The structures were solved by direct methods (SIR-92)<sup>26</sup> and refined using full-matrix least-squares

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TABLE 1. Data collection, structure solution, and refinement parameters for 1-4

Parameter	1	2	3	4
Empirical formula	C <sub>13</sub> H <sub>10</sub> O <sub>2</sub>	$C_{14}H_{14}O$	C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O	C <sub>14</sub> H <sub>14</sub> O
M	198.21	198.25	200.24	198.25
Crystal system	monoclinic	Othorhombic	Othorhombic	Othorhombic
Space group	$P2_1$	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$
a/Å	8.185(2)	6.9970(11)	5.6959(16)	5.7985(13)
b/Å	6.4760(15)	7.6398(14)	7.705(2)	7.6626(16)
c/Å	9.722(3)	20.983(4)	22.771(6)	24.464(5)
$\beta/^{\circ}$	104.760(10)	90	90	90
$V/Å^3$	498.3(2)	1121.6(3)	999.3(5)	1087.0(4)
Z	2	4	4	4
$D_c/\mathrm{g \ cm}^{-3}$	1.321	1.174	1.331	1.211
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	0.089	0.072	0.087	0.074
T/K	100(2)	100(2)	298(2)	100(2)
Crystal size/mm	$0.3 \times 0.3 \times 0.3$	$0.3 \times 0.3 \times 0.3$	$0.2 \times 0.25 \times 0.25$	$0.2 \times 0.3 \times 0.4$
$\theta$ Range/°	2.91 to 27.5	2.84 to 25.48	3.19 to 26.00	1.66 to 28.00
Reflections collected	3808	7398	6940	8605
Unique reflections, R <sub>int</sub>	1185, 0.0271	1215, 0.0372	1924, 0.0600	1520, 0.0487
Reflections with $I > 2\sigma(I)$	1145	1181	1718	1432
No. of parameters	176	192	184	192
$GOF \text{ on } F^2$	1.034	1.065	1.001	1.089
Final $R_1(F)^* (I > 2\sigma(I)) / wR_2(F^2)^*$	0.0293, 0.0302	0.0279, 0.0287	0.0386, 0.0871	0.0340, 0.0374
$R_1^{a}/wR_2(F^2)^{b}$ (all data)	0.0770, 0.0775	0.0731, 0.0735	0.0468, 0.0905	0.0862, 0.0872

 $\label{eq:R_I} \begin{array}{l} {}^{a}R_{I}\left(F\right) = \Sigma(||F_{o}| - |F_{o}||) / \Sigma|F_{o}| \\ {}^{b}wR_{2}(F^{2}) = \{\Sigma[w(F_{o}^{\ 2} - F_{c}^{\ 2})^{2}] \ / \Sigma \ [w(F_{o}^{\ 2})^{2}]\}^{\frac{1}{2}} \end{array}$ 

calculations on F<sup>2</sup> (SHELXL-97)<sup>27</sup> on all reflections. Anisotropic thermal displacement parameters were refined for all nonhydrogen atoms. Structural illustrations have been drawn with ORTEP-3 for Windows<sup>28</sup> and PLUTON.<sup>29</sup> SIR-92, SHELXL-97, ORTEP-3, and PLUTON were included in the WinGX software package.<sup>30</sup> The crystal and refinement parameters are summarized in Table 1.

## **RESULTS AND DISCUSSION**

Of the four compounds, 1, 3, and 4 are commercially available, while compound 2 was prepared through an Ullmann coupling reaction<sup>31</sup> between 2,6-dimethylphenol and bromobenzene. The yield was low, but the reaction conditions were by no means optimized. Several methods for the synthesis of 2 have been reported previously, e.g., by Niu et al.<sup>24</sup>

#### Molecular Structures and Chirality

Compound 1 (Fig. 1) is a liquid at ambient temperature, but crystallizes on cooling in space group  $P2_1$ , which is one



Fig. 1. The molecular structures of 1 (left) and 2 (right) displaying the crystallographic numbering schemes. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted. Chirality DOI 10.1002/chir

of the Sohncke space groups. Compound 2 (Fig. 1) is a crystalline solid at ambient temperature, and was also found to crystallize in a Sohncke space group  $(P2_12_12_1)$ .

From a stereochemical point of view, the two ethers are very different. Molecules of 1 are conformationally chiral in the solid state (Fig. 2), while molecules of  $\mathbf{2}$  were found to accommodate a virtually achiral conformation (pseudo-Cssymmetry) in the crystalline state. The chirality of 2 is therefore to be sought in the supramolecular structure. Well-known examples of simple achiral inorganic compounds crystallizing in Sohncke space groups include quartz, magnesium sulfate heptahydrate, strontium formate, and sodium



Fig. 2. Diagram of the molecular conformations of 1 and 2, viewed along the plane of the nonsubstituted phenyl ring and the ether link. Molecules of 1 appear as two enantiomers (left) while molecules of 2 displays a mirror plane bisecting the molecule.

chlorate<sup>32</sup> and more recently we reported chiral crystals of the achiral reagent pyridinium dichromate.<sup>33</sup> Especially the chirality of sodium chlorate crystals has attracted conside-rable interest over the years.<sup>34–38</sup> With achiral molecules, there are no enantiomers and the crystallization of **2** is perhaps better described as a spontaneous generation of chirality rather than spontaneous resolution. The crystallization of achiral organic substances as chiral crystals has been reviewed.<sup>39</sup>

Why are crystals of **2** chiral? There is one set of CH... $\pi$  interactions<sup>40</sup> in **2** that is of particular interest: the shortest contact, 2.85(2) Å, is between H3 and C13<sup>i</sup> [symmetry code: (i) -1/2+x, 1/2-y, 1-z], and the distance to the centroid of the aromatic ring is 2.80(2) Å. These interactions give rise to chains extended parallel to the *a*-axis, and these chains are folded into helices. The resulting helices are best visualized by allowing the centroid of the phenyl ring to be a member in the helix, as shown in Figure 3.

Having found that **1** and **2** crystallize in Sohncke space groups, we turned to the Cambridge Structural Database (CSD)<sup>41</sup> to find additional candidates for total spontaneous resolution. The simplest diaryl ether, diphenyl ether, crystallizes in space group  $P2_12_12_1$ ,<sup>42</sup> but its low melting point and a competing racemic polymorph is a disadvantage. Instead, we turned our attention to di(4-aminophenyl) ether, **3**, and di(*p*-tolyl) ether, **4**.

The crystal structure of **3** was previously published (except for the coordinates of most of the H atoms),<sup>43</sup> while only the cell parameters and the space group have been reported for compound **4**.<sup>44</sup> Both compounds have been reported to crystallize in space group  $P2_12_12_1$ , which we could confirm. Like the molecules of **1**, the individual molecules of **3** and **4** are conformationally chiral in the solid state (Fig. 4).

#### **Total Spontaneous Resolution**

In solution or the liquid state, fast interconversion between different chiral and achiral conformations of compounds **1–4** are expected, and no chirality is expected to persist. Therefore, these four compounds are all suitable candidates for total spontaneous resolution (Fig. 5).

The problem is to measure optical activity in the bulk samples obtained by crystallization, since only solid-state methods are useful. Using Mo-K<sub> $\alpha$ </sub> or Cu-K<sub> $\alpha$ </sub> radiation, it is



Fig. 3. Plot showing CH... $\pi$  interactions (dashed lines) in 2, generating supramolecular helices. The helix is viewed along the crystallographic *b*-axis.



Fig. 4. Molecular structure of 3 (left) and 4 (right) displaying the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The different sizes of the ellipsoids for 3 and 4 is due to the fact that data were recorded at ambient temperature for 3, but at 100 K in the case of 4. All H atoms have been omitted.



Fig. 5. Scheme displaying total spontaneous resolution of 1. If primary nucleation is slow, one enantiomorph is likely to form a crystal nucleus before the other. Secondary nucleation, i.e., the emission of small fragments from a crystal present in the solution, may ensure that all new crystals are of the same enantiomorph as the first crystal formed, if the two enantiomers interconvert rapidly in solution.

not possible to determine the absolute structure of 1-4 and it is therefore not possible to discriminate between the enantiomorphs. In our previous work on total spontaneous resolution, we relied on solid-state CD-spectroscopy,45 and it was found that single-crystals of 2 displayed circular dichroism in the solid state. This is noteworthy, since the molecules are essentially achiral and the solid-state circular dichroism has to be attributed to the crystal packing. This fact may perhaps explain the comparably low magnitude of the circular dichroism. Grinding a bulk sample homogenous and analyzing it by solid-state CD spectroscopy can provide proof for total spontaneous resolution. Indeed, when 2 was crystallized by slow evaporation of a solution in ethanol, the bulk product displayed circular dichroism of similar magnitude as single crystals, indicating substantial "crystal enantiomeric excesses" in the samples (Fig. 6). We previously reported a method for quantitative solid-state CD-spectroscopy,<sup>20</sup> but since crystals of 1-4 have no heavy atoms, no reliable Flack parameter<sup>46,47</sup> can be obtained by single-crystal X-ray diffraction.



Fig. 6. Solid-state CD spectra (KBr-matrix) for both enantiomorphs of 2. Chirality DOI 10.1002/chir

Therefore, the possibility of twinning-by-inversion cannot be excluded, and it cannot be proved that a reference crystal actually is enantiomerically pure.

No special precautions (such as stirring<sup>36</sup>) are needed to obtain optically active samples, and the enantiomorph obtained in excess is randomly distributed between different batches. Occasionally (about two batches out of ten), racemic samples were also observed. Since the distribution of enantionorphs is stochastic, it is unlikely that external influences such as cryptochirality<sup>5,21,48</sup> induce the optical activity. Since compound 1 is a liquid at ambient temperature, no solidstate CD-spectra were obtained. Instead, we attempted to trap the conformational chirality of 1 by a solid state nucleophilic addition to the carbonyl group. This would give rise a chirogenic center, and any enantiomeric excess could be determined by classical methods. We have previously shown that the reaction between solid methyllithium and chiral crystals of tris{2,6-diphenylphenolato-(p-tolylaldehyde)}-aluminum gave 1-p-tolylethanol with an enantiomeric excess of 17%.<sup>49</sup> To test this hypothesis, the reaction between 1 and solid dimethylmagnesium was investigated. This reaction, however, was found to be difficult to control. At low temperature, the reaction between carefully mixed powders of 1 and dimethylmagnesium was very slow. Four weeks at 195 K gave only traces of (racemic) product along with several unidentified by-products. Performing the reaction at 243 K did not improve the results. If the temperature was slowly increased, the reaction mixture would suddenly turn black with evolution of heat and smoke. Even at 195 K, such violent reactions could take place on vigorous grinding.

When **3** is recrystallized from methanol without stirring, a racemic product was obtained, but on stirring the product obtained is optically active, as demonstrated by solid-state circular dichroism (Fig. 7). More noteworthy is that the commercial bulk product showed a low, but still detectable, optical activity. In commercial **4**, the solid state circular dichroism was of the same magnitude as for single crystals, indicating a substantial enantiomeric excess. Upon recrystallization (with or without stirring) **4** was always obtained in an optically active form (Fig. 8) and excess of both enantiomers was obtained with similar frequency.

It has recently been reported that benzil, diphenyl sulfide, benzophenone, tetraphenylethylene, guanidine carbonate, 2,6-di-*tert*-butyl-4-methylphenol, hipuric acid, cytosine, and ninhydrin may be optically active in commercial bulk samples.<sup>50</sup> In addition to **3** and **4**, we found another three examples of "achiral" compounds commercially available in an optically active form: 2,6-diphenylphenol, 2-benzoyl pyridine, and antracene-9-carboxaldehyde (two bottles were optically



Fig. 7. Solid-state CD spectra for both enantiomorphs of 3.



Fig. 8. Solid-state CD spectra for both enantiomorphs of 4.

active, one was racemic). All attempts to react optically active 2-benzoyl pyridine or antracen-9-carboxaldehyde with solid dimethylmagnesium gave racemic products.

In conclusion, we studied four simple diaryl ethers, three of which readily underwent total spontaneous resolution. In fact, two of them were actually obtained in an optically active form in the commercial products, showing that total spontaneous resolution indeed is very spontaneous in certain cases.

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## SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article at the publisher's web-site.

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