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# Molecular Crystal Engineering by Shape Mimicry

**James K. Whitesell,* Raymond E. Davis,* Man-Shing Wong, and Ning-Leh Chang**

*Contribution from the Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712*

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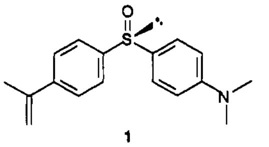
**Abstract:** Based on the high statistical preference for organics in general and true racemates in particular to pack in one of the centrosymmetric space groups, formation of molecular crystals of single enantiomers of shape-symmetric molecules was predicted to occur with approximate crystallographic symmetry. Thus, enantiomerically pure sulfoxide **1** was designed with two segments of nearly identical shape but with significantly different electron-donor/acceptor properties. Packing of **1** was predicted to occur in a near-centrosymmetric or quasicentrosymmetric fashion, with pairs of **1** arranged as would be expected for a true racemic crystal. Such a packing motif would lack true centrosymmetry and, in certain space groups, could result in a polar direction in the crystal and net additivity of the vectors from nitrogen to sulfur (the direction of polarizability for the molecules). Enantiomeric sulfoxide **1** does form molecular crystals with near centrosymmetry, mimicking $P2_1/c$, where the vector from the dimethylamino group to sulfur of one molecule is antiparallel to that from the isopropenyl group to the sulfur of the other. Thus, there is a substantial net directionality of polarizability vectors from nitrogen to sulfur in this pair. By contrast, the sulfoxides **2** and **3**, wherein the two phenyl moieties in each differ significantly in shape, form molecular crystals in which the vectors from nitrogen to sulfur are antiparallel and there is substantial net additivity of the dipole vectors from sulfur to oxygen. Crystal data for **1** at −80 °C: monoclinic, $P2_1$ (No. 4), $Z = 4$ (quasi-$P2_1/c$), $a = 7.6716(13)$ Å, $b = 8.2498(20)$ Å, $c = 26.1127(49)$ Å, $\beta = 114.716(13)°$, for data with $I > 2\sigma(I)$, $R_1 = 0.0505$, $wR_2 = 0.1059$. Crystal data for **2** at 25 °C: monoclinic, $P2_1$ (No. 4), $Z = 2$, $a = 7.8030(6)$ Å, $b = 6.0355(6)$ Å, $c = 17.037(2)$ Å, $\beta = 96.899(7)°$, for data with $I > 2\sigma(I)$, $R_1 = 0.0542$, $wR_2 = 0.1353$. Crystal data for **3** at −80 °C: monoclinic, $P2_1$ (No. 4), $Z = 2$, $a = 7.7523(8)$ Å, $b = 5.9869(7)$ Å, $c = 14.8133(16)$ Å, $\beta = 103.244(8)°$, for data with $I > 2\sigma(I)$, $R_1 = 0.0383$, $wR_2 = 0.1041$. All three structures were refined by full-matrix least-squares methods versus $|F|^2$.



**1**

## Introduction

Although the study of crystal packing has drawn considerable attention through the years for intrinsic scientific reasons as well as practical considerations, there is as yet no generally successful approach to predicting, let alone controlling, molecular orientations in crystals. Thus, the rational design and preparation of crystalline and other supramolecular materials for a wide range of applications is hampered by insufficient knowledge of those factors that control packing. As a result, whereas molecular properties have been given considerable attention in preparation of substances with desired properties, the molecular packing into supramolecular arrays such as single crystal materials has until now been left mainly to chance. In the absence of general methods for controlling multimolecular arrays, any approach that significantly alters the odds in favor of a particular packing feature represents a potential tool for engineering supramolecular arrays. Optimization of bulk properties requires tailoring of intermolecular orientations in addition to molecular properties.[1] For example, the optimal relative orientation of the polarization of the collinearly propagating waves and of molecular charge transfer axes for second-order nonlinear optics has been described,[2–5] and these properties disappear for rigorously centrosymmetric structures.

The bias for centrosymmetry is estimated to be greater than 10:1 for crystals of achiral, nonpolar organic molecules[6] and even higher for molecular crystals that contain enantiomeric pairs (racemic crystals). We recently communicated our statistical study of the influence of molecular dipoles on crystal packing, finding that for molecules that lack strong hydrogen bonding, the magnitudes of the dipoles had no significant correlation with centrosymmetry.[7] We believe, then, that molecular shape represents the dominant factor in determining the high preference for centrosymmetric alignments in most molecular crystals.[8] We suggest that the high propensity for centrosymmetry can be turned

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(6) Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates and Resolutions*; Wiley-Interscience: New York, 1981.

(7) Whitesell, J. K.; Davis, R. E.; Saunders, L.; Wilson, R., Feagins, J. *J. Am. Chem. Soc.* **1991**, *113* , 3267.

(8) The relationships of molecular shape and crystal packing are elegantly discussed in the classic text by A. I. Kitaigorodsky (*Molecular Crystals and Molecules*; Academic Press: New York, 1973). A recent study of packing energies has shown on a quantitative basis the relative importance of inversion among the symmetry operators in many organic molecular crystals; Filippini, G.; and Gavezzotti, A. *Acta Crystallogr., Part B* **1992**, *B48*, 230.

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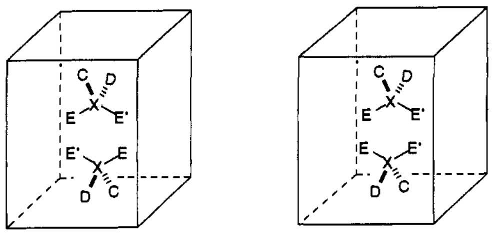

centrosymmetric packing of the racemate

pseudocentrosymmetric packing of a single enantiomer

**Figure 1.** Possible centrosymmetric packing for the racemate and quasicentrosymmetric packing for a single enantiomer of a quasisymmetric, chiral molecule.

to advantage to provide a desirable alignment of molecules that have internal quasisymmetry by virtue of the presence of groups of nearly identical shapes. Further, the resulting quasicentrosymmetry *within* a pair of molecules permits prediction, and hence tailoring, of desirable orientational aspects within that pair of molecules.

The rationale of this design method is shown schematically in Figure 1. Each molecule depicted is chiral by virtue of the presence of four different groups (E, E′, C, and D) arranged about a tetrahedral center. A possible centrosymmetric packing of such a unit with its enantiomer (i.e., the racemic crystal) is shown on the left where there is an antiparallel arrangement of all like vectors (e.g. X → C) between the pairs of molecules. A single enantiomer cannot crystallize in such a centrosymmetric arrangement. However, to the extent that the groups E and E′ are similar in shape (isosteric[9]), a packing arrangement with the vector X → E of one molecule antiparallel to the X → E′ vector of the other results in an arrangement that mimics centrosymmetry. This quasicentrosymmetric packing can result in net additivity of molecular properties (such as polarizability) so long as the properties of E and E′ differ. Thus, if the groups E and E′ are polar or polarizable to different degrees, then the directions for polarizability in the quasicentrosymmetric pair (at the right in Figure 1) will not cancel and a net polarizability for the pair will be enforced.[10] Indeed, so long as quasisymmetric molecular packing obtains, the spatial relationship of vectorial properties (e.g., X → E) of molecules so related is predictable. Within a quasicentrosymmetrically related pair, the vector X → E in one molecule is antiparallel to the X → E′ vector of the other (and vice versa), and thus the angle subtended between the X → E vectors ($\beta$) of the pair is equal to 180° − $\alpha$, where $\alpha$ is the *intra*molecular E–X–E′ angle (Figure 2).

For example, in the scenario shown in Figure 1 with ideal tetrahedral angles, the angle between the X–E bonds in the quasicentrosymmetric pair would be 71° (i.e., 180° − 109°). We report here the first example using mimicry of centrosymmetric packing to engineer the relative orientations of molecular properties within crystals.

## Results and Discussion

The sulfoxide **1**[11] was designed to have quasisymmetry, with isopropenyl and dimethylamino groups of nearly identical shapes but with significantly different electron-donating abilities. To the extent that the isopropenylphenyl and (dimethylamino)phenyl units are isosteric, **1** can mimic the shape of its own enantiomer by substituting one of these groups for the other, providing a packing arrangement with quasicentrosymmetry. Within such a packing motif, pairs of molecules would be oriented about an approximate center of symmetry, as illustrated schematically in Figure 3.

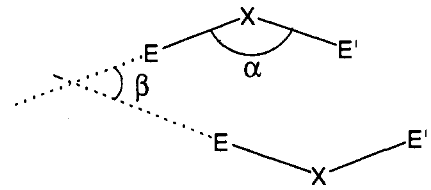

**Figure 2.**

Indeed, the (*S*)-**1** enantiomer formed molecular crystals with approximate $P2_1/c$ symmetry, with quasicentrosymmetically related pairs as shown in Figure 4.[12]

The packing arrangement with four molecules per unit cell is more complicated than that expressed by the single pair of molecules in Figure 4, containing two such pairs, with one pair related to the other by rotation-translation about a 2-fold screw axis (Figure 5).[13] The two molecules A and B are related to each other by approximate centrosymmetry, as are A′ and B′. The vectors from nitrogen to sulfur for B and B′ are coincidentally nearly perpendicular (89.3°) to the screw axis, and are thus nearly antiparallel; those for molecules A and A′ are inclined to the screw axis at 44.9° and thus combine to provide a net polar direction for the crystal.[14,15]

To further test our hypothesis that the packing arrangement for **1** was directed by quasisymmetry, we prepared[11] two additional sulfoxides, **2** and **3** (Figure 6), where the steric requirements for the substituents on the phenyl rings are now substantially different. The packing arrangements for these two sulfoxides are very similar to one another, and substantially different from that for **1**. The marked deviations from approximate centrosymmetry in these structures are illustrated by the following interplanar angles (each of which would be 0° in a centrosymmetric arrangement): the phenyl rings bearing dimethylamino groups make angles of 52.2° in **2** and 46.2° in **3**; the phenyl rings bearing alkyl groups make angles of 58.4° in **2** and 60.6° in **3**. In these structures, the vectors from nitrogen to sulfur are nearly antiparallel (177.6° in **2**, 178.3° in **3**) between the molecules comprising the unit cell

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[9] The idea that groups and molecules of similar shape and size can be substituted one for another in molecular crystals is not new. The application of quasiracemates for the assignment of absolute configuration was the first thorough study of isosteric substitution and dates from the early part of the 20th century (for a review see: Fredga, A. *Bull. Soc. Chim. Fr.* **1974**, 174). In a more recent application, "structural mimicry" was utilized to produce solid solutions of two compounds in which solid-state photoreactivities were altered (Theocharis, C. R.; Desiraju, G. R.; and Jones, W. *J. Am. Chem. Soc.* **1983**, *105*, 3606). This concept also plays an important role in pharmaceutical research, springing from Fischer's original suggestion in 1894 of a "lock and key" fit between substrates and enzymes (see: Mason, S. F. *Chemical Evolution*; Clarendon Press: Oxford, 1991; p 137).

[10] This approach does not directly control the relative spatial relationship between pairs of molecules in crystals with four (or more) molecules per unit cell. However, our finding[8] that there is no correlation between the magnitude of the molecular dipole and relative dipole orientations makes cancellation of polarizability vectors highly unlikely.

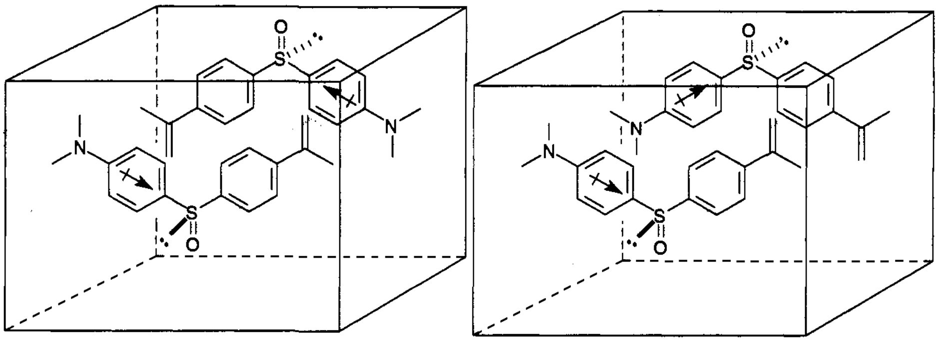
[11] Single enantiomers of **1** (as well as **2**, and **3**) of known absolute configuration, as shown, were prepared by a modification of our general procedure for the preparation of enantiomerically enriched sulfoxides. See: Whitesell, J. K.; Wong, M.-S. *J. Org. Chem.* **1991**, *56*, 4552. This significant improvement will be reported separately.

[12] The approximation to centrosymmetry is quite close, as shown by the following description. The quasi-inversion center between molecules A and B is calculated from the refined non-hydrogen crystallographic coordinates, omitting the dimethylamino and isopropenyl groups, to be at 0.5000(30), 0.5006(16), 0.2500(7). Inverting molecule A through that point gives atom positions that range from 0.016 to 0.095 Å from the refined locations of molecule B for atoms not including dimethylamino or isopropenyl groups; the only atoms within those substituent groups that differ by more than 0.095 Å from the calculated quasicentrosymmetric locations are those involving the isopropenyl double bond, C9a vs C17a (0.134 Å) and C17a vs C9b (0.204 Å).

[13] The two sulfoxide groups within each quasicentrosymmetric pair are more than 10.8 Å apart. Thus, based both on this large distance and the results of our statistical analysis,[8] it is unlikely that the polarity of that group has a significant influence on formation of the pseudocentrocymmetric pair. The closest approach of sulfoxide groups between molecules related by the pseudoglide plane is 6.8 Å; however, this distance is between two sulfur atoms and the relative orientation of the sulfur to oxygen vector is approximately 90°, so this approach cannot represent an electrostatic driving force for the packing arrangement.

[14] Second harmonic generation (frequency doubling) of 1064 m$\mu$ laser light was observed with a powdered sample of crystalline **1**. Quantitative SHG measurements are being pursued with larger, single crystals of **1**.

[15] It is important to note that any crystal in space group $P2_1$ contains a polar crystallographic axis (the *b* axis). However, this does not necessarily result in combination of molecular directions of electrostatic polarization (or polarizability) to give *significant* electrooptical bulk properties to the crystal.[1a]



**racemate**
**(centrosymmetric)**

**single enantiomer**
**(quasicentrosymmetric)**

**Figure 3.** Possible centrosymmetric packing for the racemate and quasicentrosymmetric packing for a single enantiomer of the nearly symmetric sulfoxide **1**.

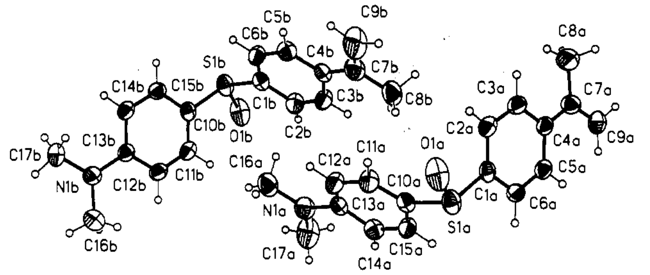


**Figure 4.** Two quasicentrosymmetrically related molecules in the structure of the *S* enantiomer of **1**. Thermal ellipsoids are shown at the 50% equiprobability level.

while those from sulfur to oxygen are not (116.0° in **2**, 114.4° in **3**) (Figures 7 and 8). As for sulfoxide **1**, the molecular crystals of enantiomeric **2** and **3** also have net polar directions, but now resulting from additivity of the sulfoxide moieties. Thus, arguments based solely upon the electrostatic interactions cannot simultaneously rationalize all three structures.

The polar direction in the molecular crystals of **1**–**3** follows from the fact that all three are single enantiomers and thus can only give noncentrosymmetric molecular crystals.[16] However, as mentioned above, it is possible to predict from molecular geometries the angular relationship between molecular vectors within a pair of molecules that are pseudocentrosymmetrically related in the unit cell. For sulfoxide **1**, the C–S–C angle is somewhat smaller, resulting in an angle of 77° between the nitrogen-to-sulfur directions of the pair. For sulfoxides **2** and **3**, it is the S–O vectors that are related by this angle. The angle $\beta$ is thus tuneable on a molecular basis by adjusting $\alpha$. We are currently preparing examples in which $\alpha \approx 180°$, for which we predict $\beta \approx 0°$, a nearly parallel orientation.[17]

In conclusion, we have successfully designed molecular features that lead to predictable features in the packing motif with net summation of a molecular property from the molecules comprising the molecular crystal.[18] We believe that these results have significant implications for the design of materials for applications requiring molecular crystals with a polar direction as well as in other areas of materials science that require control of molecular orientations within multimolecular aggregates. Furthermore, utilization of molecular shape as a major and controllable determinant of orientation in molecular crystals will provide an avenue for developing additional, fundamental concepts of crystal packing.

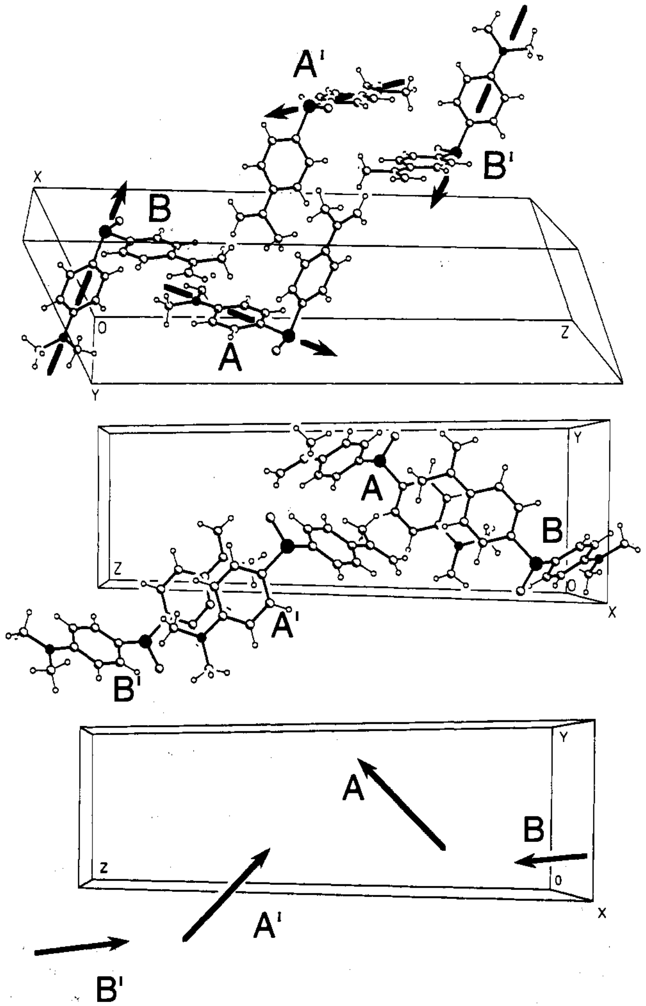


**Figure 5.** The four molecules per unit cell in the structure of the *S* enantiomer of **1**, viewed (a, top) approximately along the *y* axis and (b, middle) approximately along the *x* axis. (For clarity, N and S are shown as solid spheres.) Molecules A and B are related by an approximate inversion center, as are A′ and B′. Molecules A and A′ are related by the 2-fold screw axis of space group $P2_1$, as are B and B′; molecules A and B′ are approximately related by the pseudo-*c*-glide plane of space group $P2_1/c$, as are A′ and B. Directions of the N → S vectors are emphasized as bold arrows in parts a and c. Note that the N → S vectors of A and A′ have a net component parallel to the +*y* axis, whereas the B and B′ vectors are nearly antiparallel.

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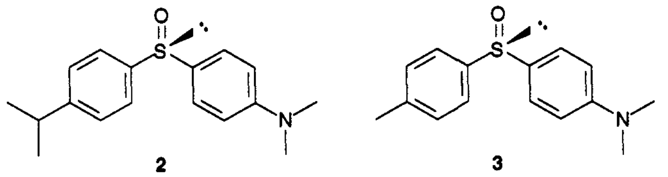
[16] Strictly speaking, not all crystals belonging to noncentrosymmetric space groups necessarily exhibit second-order, nonlinear effects and indeed, crystals belonging to the noncentrosymmetric point group 432 cannot, by symmetry. Though no crystallographic axis in a crystal of point group 222 is polar, the relationship between the single nonvanishing $d_{XYZ}$ coefficient and the unique non-zero one-dimensional $\beta$ tensor coefficient shows that NLO effects are permitted in this crystal class, that is, polar directions are possible (e.g., see ref 1d, p 337); this point group includes space group $P2_12_12_1$, one of the statistically most frequent among molecular crystals.

[17] These arguments specifically address the relative relationships *within* a pair of molecules. They do not apply to the relationship between pairs of molecules where the effects of a second quasicentrosymmetric pair *could* cancel the effects of the first. Such is not the case in the structure described here. In fact, the relationships *between* pairs in the single enantiomer crystal differ markedly from those of the racemate.



2 3

Figure 6.

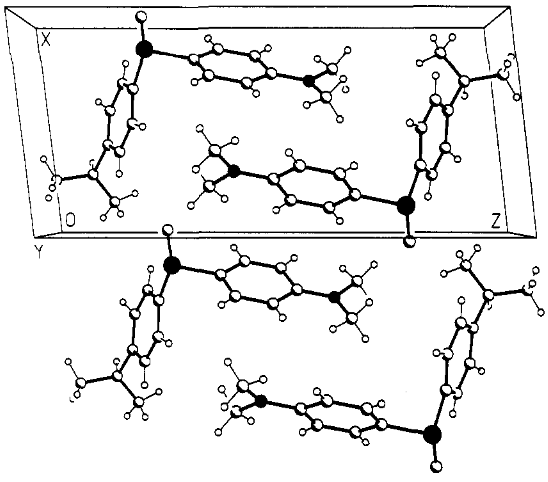


**Figure 7.** Packing diagram of the *S* enantiomer of **2**. Here all molecules are equivalent by the symmetry of space group $P2_1$, with, e.g., the top two molecules related to one another by the symmetry of the screw axis.

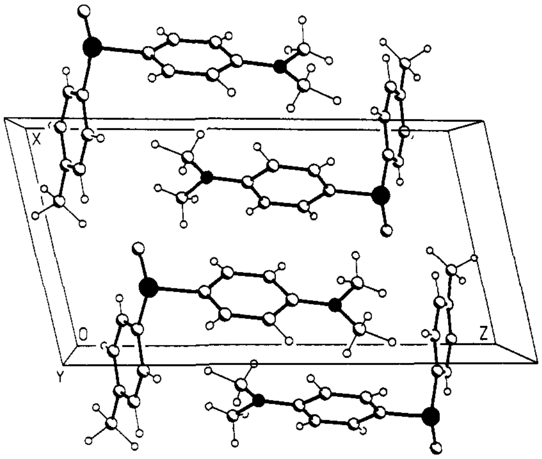


**Figure 8.** Packing diagram of the *S* enantiomer of **3**. Here all molecules are equivalent by the symmetry of space group $P2_1$, with, e.g., the top two molecules related to one another by the symmetry of the screw axis.

## Crystallographic Analysis.

For each substance, a single crystal was affixed to a glass fiber attached to a goniometer head and then transferred to a Siemens R3m autodiffractometer. Crystals of **1** and **3** were maintained in a cold (−80 °C) stream of dry nitrogen for the duration of the diffraction experiments. Numerous crystals of **2** cracked upon being cooled, so the diffraction experiments for that compound were carried out at ambient temperature. Preliminary diffraction studies allowed determination of crystal symmetry and verification of the suitable quality of the crystals for intensity data collection. A summary of the crystal data and structure refinement is presented in Table 1.[19] The measured intensities were reduced and assigned standard deviations.

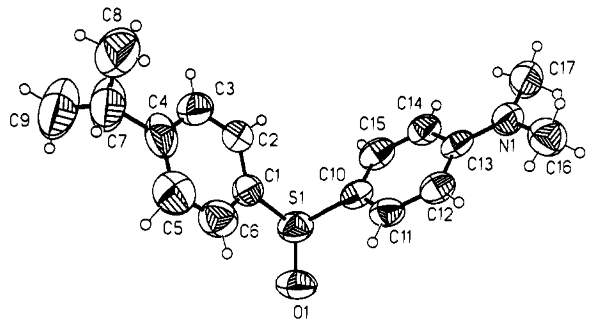


**Figure 9.** One molecule of the *S* enantiomer of **2**, with 50% equiprobability ellipsoids.

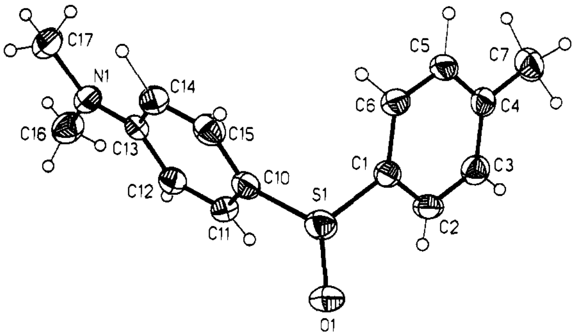


**Figure 10.** One molecule of the *S* enantiomer of **3**, with 50% equiprobability ellipsoids.

**Table 1.** Crystallographic Data

| compound | 1 | 2 | 3 |
|---|---|---|---|
| chem formula | $C_{17}H_{19}ONS$ | $C_{17}H_{21}ONS$ | $C_{15}H_{19}ONS$ |
| fw | 285.40 | 287.42 | 259.37 |
| temp, °C | −80 | 25 | −80 |
| crystal system | monoclinic | monoclinic | monoclinic |
| space group | $P2_1$ (No. 4) | $P2_1$ (No. 4) | $P2_1$ (No. 4) |
| *a*, Å | 7.6716(13) | 7.8030(6) | 7.7523(8) |
| *b*, Å | 8.2498(20) | 6.0355(6) | 5.9869(7) |
| *c*, Å | 26.1127(49) | 17.037(2) | 14.8133(16) |
| *β*, deg | 114.716(13) | 96.899(7) | 103.244(8) |
| *V*, Å$^3$ | 1501.26(53) | 796.56(13) | 669.30(13) |
| *Z* | 4 | 2 | 2 |
| $d_{calcd}$, g·cm$^{-3}$ | 1.263 | 1.198 | 1.287 |
| radiation | Mo K$\alpha$, 0.71069 | Mo K$\alpha$, 0.71069 | Mo K$\alpha$, 0.71069 |
| abs coeff, $\mu$(Mo K$\alpha$), cm$^{-1}$ | 2.01 | 1.90 | 2.19 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$][a] | 0.0505, 0.1059 | 0.0542, 0.1353 | 0.0383, 0.1041 |
| $R_1$, $wR_2$ for all data | 0.0962, 0.1292 | 0.0722, 0.1507 | 0.0395, 0.1054 |

[a] The function minimized was $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2)^2]^{1/2}$; $R_1 = \sum |(|F_o| - |F_c|)| / \sum |F_o|$.

The structures were solved by direct methods, using the program SHELXTL-PLUS.[20] Because of the near-centrosymmetry of crystals of **1**, that structure was solved in space group $P2_1/c$. However, molecular crystals of this single enantiomer could not be centrosymmetric. Thus, the inversion center was removed, the origin was shifted to the conventional setting of $P2_1$, and the atom identities were assigned commensurate with the absolute stereochemistry known from the synthesis. All structures were then refined by full-matrix least-squares methods versus $|F|^2$ with the program SHELXL-93.[21] Neutral atom scattering factors were used, including real and imaginary corrections for anomalous dispersion. As expected, refinement of **1** by conventional crystallographic least-squares methods versus $|F|$ was extremely troublesome, due to high parameter correlations resulting from the approximate symmetry. These difficulties were overcome with the use of a restrained refinement versus $|F|^2$ implemented

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(18) We do not mean to imply that molecular crystals have not heretofore been observed with pseudosymmetric packing of a single enantiomer, similar to the centrosymmetric arrangement of the racemate. For an interesting example see: Ohashi, Y.; Kazunori, Y.; Kurihara, T.; Sasada, Y.; Ohgo, Y. *J. Am. Chem. Soc.* **1982**, *104*, 6353. Dunitz, J.; Uchida, A. *Acta Crystallogr.* *B46* **1990**, 45.

(19) Full details of the data collections and structure refinements appear in the Supplementary Material.

(20) Sheldrick, G. M. *SHELXTL-PLUS* (Version 4.11); Siemens X-Ray Analytical Instruments, Inc.: Madison, WI, 1991.

(21) Sheldrick, G. M. *J. Appl. Crystallogr.*, in preparation.

by the program SHELXL-93.[22] From this refinement we could clearly distinguish, on the basis of bond length differences, between $C{=}CH_2$ and $C{-}CH_3$ in the isopropenyl group of **1**, even before the location of hydrogen atoms. For all three structures, hydrogen atom positions were calculated in ideal positions, and these locations were confirmed in difference electron density maps. All hydrogen atom positions in **1** and **2** were refined with H riding on C. In the refinement of **1**, and again in that of **2**, hydrogen atoms on $sp^2$ carbons were restrained to identical thermal parameters, as were those on $sp^3$ carbons. In **3**, it was possible to refine independent hydrogen positional and thermal parameters for the phenyl hydrogens, while those for the nine aliphatic hydrogens were restrained to be equal. Thermal ellipsoid plots of **1**, **2**, and **3** appear in Figures 4, 9, and 10, respectively.

**Acknowledgment.** Financial support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant ACS-PRF AC-20714 to J.K.W,), the Robert A. Welch Foundation (F-626 to J.K.W. and F-233 to R.E.D.), the National Science Foundation (Grant DMR-9014026 to J.K.W.), and the Advanced Research Program of the Texas Higher Education Coordinating Board (Grant 277 to J.K.W. and R.E.D.) is gratefully acknowledged.

**Supplementary Material Available:** Tables of crystal data and structure refinement details, fractional atomic coordinates and isotropic (or equivalent isotropic) thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, bond lengths and bond angles for non-hydrogen atoms (16 pages); tables of observed and calculated structure factor amplitudes (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(22) We are grateful to Professor George Sheldrick for generously carrying out a preliminary restrained refinement of **1** with a development version of SHELXL-93 when the program was not yet available for distribution. All three structures have now been refined in Austin with the public domain version of the program. Restraints on the refinement of **1** are summarized as follows, with SHELXL-93 commands indicated (refer to Figure 4 for atom identifications): (a) chemically equivalent 1–2 and 1–3 distances in the two molecules were restrained (SAME) to agree (with esd's of 0.02 and 0.03 Å, respectively), except for the $-CH_3$ and $=CH_2$ carbons of the isopropenyl groups, which were allowed to refine freely so that the C—C distances could be used to check their assignments; (b) 1–2 and 1–3 distances in each phenyl ring were restrained (SAME) to have "mirror" symmetry (with esd's of 0.02 and 0.03 Å, respectively)—e.g., C1a–C2a and C1a–C6a were restrained to agree, as were C1a⋯C3a and C1a⋯C5a; (c) the four $N{-}C_{Me}$ bond lengths were restrained (SADI) to agree (with esd's of 0.02 Å); (d) the four 1–3 distances involving phenyl carbon to $(CH_3)_2N$ carbon (e.g., C13a⋯C16a) were restrained (SADI) to agree (with esd's of 0.03 Å); (e) the two methyl carbon 1–3 distances in $(CH_3)_2N$ were restrained (SADI) to agree (with esd's of 0.03 Å); (f) atoms related by the approximate inversion center were constrained (EADP) to have the same $U_{ij}$ values.