by a small amount of the exterior electron density which is about 1–10% for every molecular orbital. This extreme sensitivity of Penning ionization to the exterior electron densities can be summarized as the stereoelectronic effect of exterior electrons in individual molecular orbitals.

The present model of calculating the orbital activity is satisfactory to make a quantitative connection between theory and experiment for branching ratios in Penning ionization. Further experimental developments involving anisotropic factors and the velocity dependence of metastable atoms will make it possible to probe the electron density of the individual MO as a function of various parts of the molecule. Penning ionization electron spectroscopy is very useful not only for probing spatial distributions of individual molecular orbitals from a quantum chemical point of view but also for understanding chemical properties of molecules, because electron densities of orbitals at the very frontier of the molecules should play important roles in chemical reactions.

Acknowledgment. We thank Professor Suehiro Iwata for providing us with his program of the ab initio MO calculations, K. Imai for his help in the experiments, and S. Matsumoto for his help in the calculations.

Chiral Discrimination in Crystalline Tri-*o*-thymotide Clathrate Inclusion Complexes. Chemical and Crystallographic Studies

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Abstract: Crystallization of tri-*o*-thymotide (TOT) from solutions of appropriate racemic guest species affords chiral single crystals of clathrate inclusion complexes in which the guest enantiomers are incorporated to different degrees. Channel-type complexes (space group $P6_1$) or cage-type complexes ($P3_121$) are obtained. The extracted guest from single crystals of the former has uniformly low, but significant, enantiomeric excess, while this excess (ee) in the latter varies widely. The highest enantiomeric purities were observed for 2,3-dimethyl-*trans*-oxirane (47%), 2,4-dimethyl-*trans*-oxetane (38%), and 2-bromobutane (37%). Larger scale resolutions of chiral guests are possible by crystallization following seeding solutions of racemic guest and TOT with powdered single crystals of clathrate. Guests with appreciably enhanced optical purity can be obtained by repeated TOT enclathration using a partially enriched guest (an unexpectedly high chiral amplification was observed in a channel complex). The TOT optical rotation, + or −, and dominant guest chirality, *R* or *S*, were determined for each clathrate, and correlations between guest chirality and TOT absolute configuration were found, e.g., all (*S*)-2-haloalkanes crystallize preferentially with *P*-(+)-TOT. TOT clathrates may thus be used for guest configurational assignments. Crystal structure analyses of *M*-(−)-TOT·(*R*)-2-bromobutane, *M*-(−)-TOT·(*R*,*R*)-2,3-dimethyl-*trans*-oxirane, the *P*-(+)-TOT·(*S*,*S*)-2,3-dimethyl-*trans*-thiirane clathrates, and the *P*-(+)-TOT·2,3-dimethyl-*trans*-thiirane clathrate containing a 1:2 ratio of the *R*,*R* and *S*,*S* enantiomers provided cage dimensions and geometry (an ellipsoidal, 2-fold symmetric cavity). Evidence that chiral discrimination is accounted for by the intermolecular interactions in the crystal has been obtained, and therefore the crystal structures also define the discriminating interactions between TOT host molecules and the more favored and less favored guest enantiomers. It is not possible to predict the preferred guest enantiomer solely by considering the van der Waals contacts between guest enantiomers and closest host atoms, but the crystal structure analyses help clarify some of the factors that govern chiral discrimination in TOT clathrates.

Introduction

One of the properties of biological systems that has long fascinated chemists is the extraordinarily high degree of chiral discrimination that such systems display when they interact with racemic substrates. In recent years, many ingenious chemical approaches have been taken that seek to mimic these properties. The motivation for this work has been both fundamental, to better understand the features that control chiral interactions, and practical, to obtain efficient enantiomer resolutions; many notable achievements have been reported.[2]

The inclusion complexes of tri-*o*-thymotide (TOT; Figure 1) provide a possible medium for reactions of included guest molecules and present an attractive system for studying molecular and, especially, chiral recognition. The previously reported[3] ability of TOT to form clathrates[4] with a wide variety of guest molecules, many of which crystallize in chiral (cage and channel type)

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(1) (a) Weizmann Institute of Science. (b) Israel Institute for Biological Research. (c) Laboratoire de Physique, Centre Pharmaceutique.

(2) (a) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1978**, *11*, 8. (b) Lehn, J. M. *Pure Appl. Chem.* **1979**, *51*, 979. (c) Gil-Av, E.; Nurok, D. *Adv. Chromatogr.* **1974**, *10*, 99. (d) Wulff, G.; Sarhan, A.; Zabrocki, K. *Tetrahedron Lett.* **1973**, 4329. (e) Baba, N.; Matsumura, Y.; Sugimoto, T. *Ibid.* **1978**, 4281. (f) Tabushi, I. *Acc. Chems. Res.* **1982**, *15*, 66.

(3) (a) Baker, W.; Gilbert B.; Ollis, W. D. *J. Chem. Soc.* **1952**, 1443. (b) Newman, A. C. D.; Powell, H. M. *Ibid.* **1952**, 3747. (c) Lawton, D.; Powell, H. M. *Ibid.* **1958**, 2339.

(4) Powell originally used the term *clathrate* only for those complexes where the guest molecules are surrounded on all sides by host molecules. He avoided its use for channel complexes. Later, however, most workers used the term *clathrate* and *inclusion complex* either as synonyms or, together, as a generic term for crystalline host–guest complexes wherein voids within the packing arrangement of the host (a packing arrangement that is generally only possible in the presence of the guest) are occupied by guest molecules. The term has also been generally implied to indicate a broader phenomenon than a simple solvate, in that many different guests can be accommodated within these voids. We favor the use of *clathrate*, or *clathrate inclusion complex*, for this entire class of molecular complexes and then *cage*, *channel*, or other descriptor. Other descriptors may be required as, for example, in the TOT·stilbene and related clathrates,[8] where the guests are contained in separate cages that are connected to one another to form a channel.

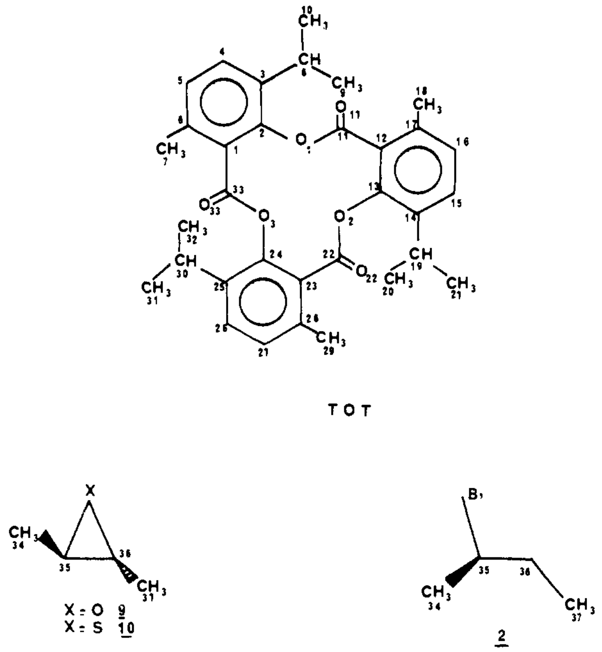

Figure 1. Structure of tri-*o*-thymotide (TOT) and the guest molecules **2**, **9**, and **10**. Atom numbering is that used in crystallographic analyses.

structures, as well as the ease of assessing the optical sign of spontaneously resolved TOT all enhanced our interest in these compounds.

In this paper we present our combined crystallographic and chemical data and attempt to account for the features that control the observed chiral discrimination. Unlike the majority of systems being studied which differentiate between enantiomers,[2] the TOT system has the advantage of allowing a precise view of the host–guest geometry and interactions by crystallographic methods.

Results and Discussion

In solution, TOT exists primarily in a chiral, propeller-like conformation that undergoes rapid interconversion between P (right-handed) and M (left-handed) forms, the activation energy for enantiomerization being ~21 kcal/mol.[5] In its guest-free form, TOT crystallizes in the achiral structure $Pna2_1$ containing equal amounts of the P and M forms.[6] However, upon cocrystallization with compounds with which it forms clathrate inclusion complexes (more than 100 different guests have afforded complexes), TOT often undergoes spontaneous resolution, i.e., any single crystal contains only P or only M configurated TOT host molecules. The TOT complexes are commonly of either the cage type, having a host:guest ratio of 2:1, each guest being surrounded by eight TOT molecules, or of the channel type, the host:guest ratio depending on the length of the guest. Small molecules, those containing up to six non-hydrogen atoms, tend to adopt cage structures while long-chain molecules generally give rise to channel complexes.[7]

The chiral discrimination experiments described here involve a variety of guest molecules that lack the functional groups generally required to achieve resolution via diastereomeric interactions. Examples of both cage and channel clathrates are included. This study sought to determine (1) the enantiomeric excess for each guest in single clathrate crystals and (2) the relative configurations of TOT and the predominant guest in each crystal.

Table I. Enantiomeric Excess of Guest and Correlation of Guest and Host Chirality in P-(+)-TOT Clathrate Crystals

guest's no.	guest	clathrate type[a]	guest[b] ee, %	guest config
1	2-chlorobutane	cage	32	S-(+)
2	2-bromobutane	cage	37	S-(+)
3	2-iodobutane	cage	<1	c
4	2-chlorooctane	channel	4	S-(+)
5	2-bromooctane	channel	4	S-(+)
6	3-bromooctane	channel	4	S-(+)
7	2-bromononane	channel	5	S-(+)
8	2-bromododecane	channel	5	S-(+)
9	*trans*-2,3-dimethyloxirane	cage	47	S,S-(−)
10	*trans*-2,3-dimethylthiirane	cage	30	S,S-(−)
11	*trans*-2,4-dimethyloxetane	cage	38	d
12	*trans*-2,4-dimethylthietane	cage	9[e]	d
13	propylene oxide	cage	5	R-(+)
14	2-methyltetrahydrofuran	cage	2	S-(+)
15	methyl methanesulfinate	cage	14	R-(+)
16	2,3,3-trimethyloxaziridine	cage	7	d
17	ethyl methyl sulfoxide	cage	80[f]	R-(+)

[a] Cage type clathrates have space group $P3_121$ ($P3_221$), while channel type clathrates have space groups $P6_1$ ($P6_5$) or $P3_1$. In the latter case, the space group depends on the length of the included guest and does not involve major changes in host packing. [b] Precision of measurement is 10% when the ee is larger than 10%; the maximum absolute error is ±1% (see Experimental Section). [c] The optical purity of the guest was nearly zero even when very large clathrate crystals were chosen to ensure an adequate quantity of guest. The reason for this is not yet clear; perhaps it is related to the low occupancy of 3 (guest:host, 1:4). [d] Absolute configuration not yet established. [e] Enantiomeric excess based upon only one crystal. [f] Reference 24b.

A typical experiment involved the following procedure: TOT was dissolved by warming in a large excess of racemic guest (all of the guests described here are liquids at room temperature), and the solution was slowly cooled. The resulting single crystals were characterized as comprising P-(+)- or M-(−)-TOT[9] by taking a 0.5–1-mg chip from each crystal, dissolving it in chloroform at ca. − 10 °C, and then measuring the optical rotation at ca. 2 °C. The rotation of TOT, $[\alpha]_D$ ~70°,[3b] and the slow rate of racemization at this temperature[5] allow the sign to be determined unambiguously on samples of this size. The solutions were then allowed to warm to room temperature, and the optical rotations were observed to fall to zero: the contribution of the guests to the optical rotation of the solution is negligible because of their low concentration (weight ratio, TOT:guest ~10:1).

The chirality and enantiomeric excess of the guest included in a clathrate crystal were determined by several different methods: direct VPC analysis of the guest[10] or of a suitable derivative[11] on chiral phases, NMR using a chiral shift reagent,[12] or, for large crystals (50–100 mg), polarimetric measurements. In some cases, large single crystals (up to 0.5 g) were prepared by repeatedly seeding a hot, saturated solution of TOT in the guest with single clathrate crystals and slowly cooling the solutions.

The enantiomeric excess of enclathrated guest and the correlation of chirality of TOT and the major enantiomer were established on "enantiomeric" systems, e.g., (+)-TOT·excess S guest and (−)-TOT·excess R guest; the observed reproducibility of the values thus assured that extraneous chiral impurities were not introduced. The results are presented in Table I.

Chiral Discrimination in Cage and Channel Clathrates. The channel clathrates display uniformly low, but measurable and significant, chiral discrimination while in the cage clathrates discrimination varies widely, the values ranging from 2% to 46% ee (the latter value signifies an enantiomer ratio of 73:27). In the channel clathrates the guests are expected to be severely

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(5) Downing, A. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc. B* **1970**, 24.

(6) Brunie, S.; Tsoucaris, G. *Cryst. Struct. Commun.* **1974**, *3*, 481.

(7) At least six additional clathrate types, including achiral crystals, are now known to be possible with TOT; four of these have already been mentioned in previous work (see ref 8, and footnote 45 therein). Other TOT complexes belong to space group $P2_1$, containing meso-2,3-butanediol carbonate, and *Pbca*, containing fluothane. The choice of clathrate depends primarily on the guest.

(8) Arad-Yellin, R.; Brunie, S.; Green, B. S.; Knossow, M.; Tsoucaris, G. *J. Am. Chem. Soc.* **1979**, *101*, 7529.

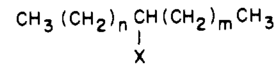
(9) (a) Arad-Yellin, R.; Green, B. S.; Knossow, M.; Tsoucaris, G. *Tetrahedron Lett.* **1980**, *21*, 387. (b) Gerdil, R.; Allemand, J. *Ibid.* **1979**, 3499. (c) Allemand, J.; Gerdil, R. *Cryst. Struct. Commun.* **1981**, *10*, 33.

(10) Schurig, V.; Burkle, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 132.

(11) Weinstein, S.; Feibush, B.; Gil-Av, E. *J. Chromatogr.* **1976**, *126*, 97.

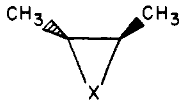
(12) Sullivan, G. R. *Top. Stereochem.* **1978**, *10*, 287.

Chart I

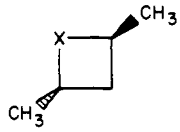


$CH_3(CH_2)_n\underset{X}{\underset{|}{C}}H(CH_2)_mCH_3$

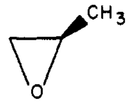
	1	2	3	4	5	6	7	8
X	Cl	Br	I	Cl	Br	Br	Br	Br
m	0	0	0	0	0	1	0	0
n	1	1	1	5	5	4	6	9



9 X = O
10 X = S



11 X = O
12 X = S



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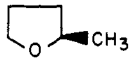
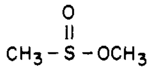
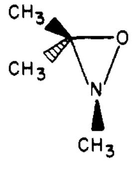


14

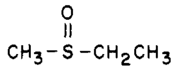


$CH_3-\overset{O}{\overset{\|}{S}}-OCH_3$

15



16



$CH_3-\overset{O}{\overset{\|}{S}}-CH_2CH_3$

17

disordered: coincidence of guest symmetry and cavity symmetry is not possible; the guests can be packed head-to-head and/or head-to-tail and may be randomly oriented in the cylindrical channels; register between the contents of different channels is unlikely. It may be considered remarkable that chiral discrimination is observed to any degree in view of the many sources of disorder.

It is noteworthy that the molecules that contain 2-fold symmetry axes, **9**–**12**, tend to afford the higher enantiomeric purities. Since the cage cavity contains a 2-fold axis, coincidence of guest molecular symmetry with host cavity symmetry is possible for these guests, and this greater order may contribute to the higher values.[13] Guests **1**–**3** and **13**–**17** (Chart I) all have the same molecular symmetry (C_1) and must be disordered in the cage cavities; they display widely varying enantiomeric purities. The lowest optical resolution values are obtained for the extremes in size (van der Waals volume) of the guest. The low value for the smallest guest studied, **13**, may be understood in terms of looseness of fit of the guest in the cavity, whose flexibility is limited (see below), but the low values for the largest guests, **3** and **14**, are not easily rationalized without additional structural data. Compounds **15** and **16** have chiral centers on sulfur and nitrogen, respectively, and are resolvable because of the high barriers to sulfur and nitrogen inversions[14] in these compounds.

The high degree of chiral discrimination with guests **1** and **2** is especially noteworthy. *sec*-Butyl groups often display methyl-ethyl disorder,[15] and chloro-methyl or bromo-methyl disorder in **1** and **2**, respectively, might also be expected on the basis of their similar van der Waals radii and observed disorder in other systems.[16] We return to this in the discussion of the clathrate structures.

Correlation of Guest-Host Configuration. Powell first pointed out that TOT enclathration might be used to establish the absolute configuration of guests.[17] There is, indeed, a remarkable correlation of configuration among all the comparable guests. Thus, for all the 2-haloalkanes examined, the *S*-(+) guests are preferentially enclathrated by *P*-(+)-TOT.[18] Arrangement of guests **2**, **15**, **9** and **10** in similar, stereochemically favored conformations (Figure 2), leads one to expect that (*S*)-**2**, (**R**)-*15*, (*S*,*S*)-**9**, and (*S*,*S*)-**10** would all be preferentially enclathrated by TOT of the same chirality and, indeed, all do preferentially crystallize with *P*-(+)-TOT. Further, as will be seen below, the methyl groups occupy nearly identical positions in the cage, and the "protruding atoms", bromine, oxygen, oxygen, and sulfur, respectively, are all located at the same site in the cage (Figure 4).

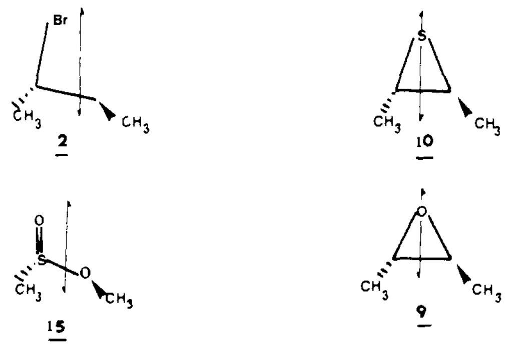


Figure 2. Enantiomers of guest molecules **2**, **9**, **10**, and **15**, which are preferentially included in a clathrate crystal built of *P*-(+)-TOT molecules. The guests are presented in orientations that they adopt relative to the 2-fold axis of the cage cavity (cf. Figure 4).

Since there are no covalent or ionic bonds linking host and guest, the clathrate cavities should be especially sensitive to the shape and volume of the guest at the chiral center(s) and not solely to the functional groups. The correlation of configuration between guests such as **15** and the halobutanes **1** and **2** suggests that many additional guest molecules, whose absolute configurations have not yet been established and for which configurational assignment would be difficult by other methods, may be readily assigned configuration through TOT enclathration. This is especially of interest for small, volatile substances lacking the functional groups generally used for derivatization with a chiral additive of known configuration. Application to hydrocarbons and halocarbons can be envisaged. The widely used chiral inhalation anesthetic halothane, for example, lacks configuration assignment; a complex with TOT has been reported.[19]

Assignments of absolute configuration by means of TOT structures rely on the hypothesis that the correlation of the absolute configurations of the host and the preferred guest enantiomer is an intrinsic property of the complex and remains unchanged in every single crystal of a given clathrate. As one test of this hypothesis, we attempted to grow TOT clathrates containing an excess of "unnatural" enantiomer, i.e., (+)-TOT·(+)-(*R*,*R*)-**9** (this complex is never observed to predominate on spontaneous crystallization from TOT and racemic **9**). In this experiment, single crystals of (+)-TOT·(−)-(*S*,*S*)-**10** were used to seed saturated solutions of TOT in (+)-(*R*,*R*)-**9**. The (+)-TOT seed might have continued to grow and incorporate (+)-TOT and the only available guest, (+)-(*R*,*R*)-**9**. However, the seed crystals failed to grow,

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(13) Coincidence of guest and cavity symmetries may not lead to greater order in all cases, but this proves to be true in these cases.

(14) Lehn, J. M. *Fortschr. Chem. Forsch.* **1970**, *15*, 311.

(15) (a) Benedetti, E.; Pedone, C.; Sirigu, A. *Acta Crystallogr., Sect. B* **1972**, *B29*, 730. (b) Addadi, L.; Ariel, S.; Lahav. M.; Leiserowitz, L.; Popovitz-Biro, R.; Tang, C. P. *Chem. Phys. Solids Their Surf.* **1980**, *8*, 202.

(16) (a) Krigbaum, W. R.; Wildman, G. C. *Acta Crystallogr., Sect. B* **1971**, *B27*, 2353. (b) Clews, C. J. B.; Cochran, W. *Acta Crystallogr.* **1948**, *1*, 4.

(17) Powell, H. M. *Nature* (*London*) **1952**, *170*, 155.

(18) Although it is convenient and satisfying that the 2-haloalkanes that crystallize in cage complexes and those that crystallize in channel complexes give the same chirality correlation, it should be emphasized that this may be fortuitous. We would anticipate that all cage-complexed guests that may be stereochemically correlated (e.g., (*S*)-**1**, (*S*)-**2**, (*R*)-**15**) would preferentially occupy the same chiral TOT cavity and, similarly, that within the series of guests adopting channel-type clathrates, stereochemically related enantiomers would complex with the same TOT chirality. However, there is no reason to expect a priori that the cage and channel cavities constructed by (+)-TOT should necessarily enclathrate the same enantiomer configuration of all the 2-haloalkanes.

(19) Wu, N. M.; Barrett, D. W.; Koski, W. S. *Mol. Phys.* **1973**, *25*, 437. This complex is, unfortunately, achiral,[7] but perhaps it will be possible to induce a different, chiral clathrate crystal structure by appropriate seeding.

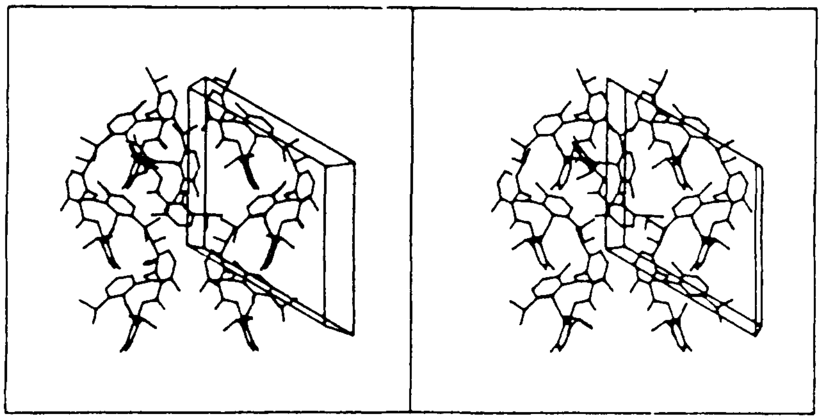

Figure 3. Stereoview of the TOT molecules that build the walls of the cage. The molecules are viewed down the *c* axis, and the top molecule has been removed for clarity. (The stereoview was drawn by using PLUTO).[54]

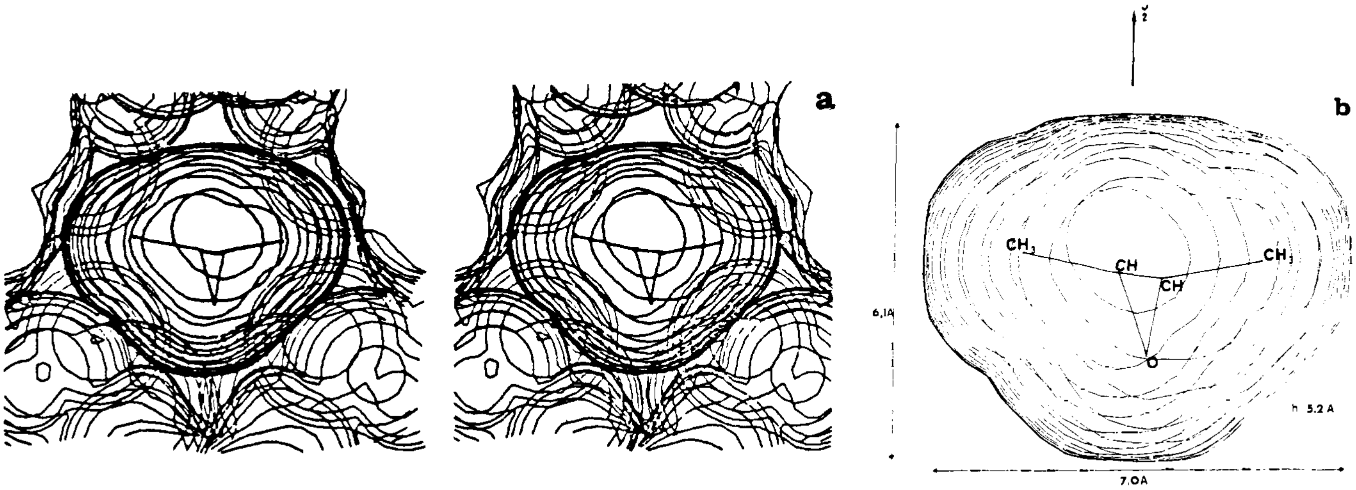

Figure 4. (a) Stereoview of the contours of the van der Waals envelope of TOT (light lines) and of the van der Waals envelope of the volume accessible to guest atoms, (heavy lines), viewed along the *c* axis. Sections are plotted every 0.3 Å, parallel to the *ab* plane, in a cube having 9.2-Å sides and centered on (0,0.33,0.1667). The position of (+)-(*R*,*R*)-2,3-dimethyloxirane is shown. (b) Dimensions of the van der Waals envelope of space available to guest; sections and guest are drawn as in a.

and a powder of clathrate crystals, comprised of (−)-TOT·(+)-(*R*,*R*)-**9**, a complex of chirality opposite to that of the seed crystals, precipitated. This result implies that formation of inclusion complexes with an intrinsically less favorable guest enantiomer as the sole included species is not possible, at least for a guest for which chiral discrimination is substantial. In cases where discrimination is very weak, perhaps both complexes may be observed.[9b]

This last experiment is also relevant to the question of the nature of the mechanism of control over crystal growth and guest inclusion. The fact that one cannot "force" the (+)-TOT host lattice to incorporate a predominance of the less favored enantiomer suggests that thermodynamic rather than kinetic factors control both the enantiomer ratios and the correlations, and that the final state, as observed by X-ray crystallography, may be used for calculations and inferences about the chiral discrimination of clathrate inclusion complexes. It should be mentioned that clathrate crystals may contain defects the presence of which might allow relief of the strain associated with the incorporation of the intrinsically less favorable guest enantiomer. Their presence might affect both the chemically and crystallographically measured ee.

Structural Data. X-ray structural analyses of four cage clathrates were performed. Cage complexes were chosen rather than the channel complexes because of the wider variation in chiral discrimination and the more ordered structures expected for them.

X-ray data were collected on crystals grown from enantiomerically pure *trans*-(*R*,*R*)-(+)-2,3-dimethyloxirane (**9**), enantiomerically pure *trans*-(*S*,*S*)-(−)-2,3-dimethylthiirane (**10**), racemic *trans*-2,3-dimethylthiirane (**10**), and 37% enantiomerically enriched 2-bromobutane (**2**); the crystallographic data are summarized in Table II. The TOT host structures are isomorphous for all of these crystals as well as for the other known cage-type clathrates.[20] The clathrate cavity is comprised of eight TOT

Table II. Crystal Data, Measured at −50 °C, for Cage-Type Clathrates

	guest			
	2^a	10^b	10^c	9^c
$a = b$, Å	13.721 (4)	13.611 (3)	13.603 (8)	13.484 (2)
c, Å	30.242 (9)	30.34 (7)	30.44 (3)	30.44 (1)
V, Å^3	4917	4861	4850	4797
$F(0,0,0)$	1896	1836	1836	1812
μ(Cu Kα), cm^{-1}	12.17	8.42	8.43	5.74
d_m, g cm^{-3}	1.191	1.158	1.163	1.154
d_c, g cm^{-3} ^{d}	1.195	1.161	1.168	1.157
Z^e	6	6	6	6
θ_{max}, deg	55	65	65	65
measd unique rfltns	2397	3145	3143	3008
obsd rfltns ($I > 2\sigma(I)$)	2090	2714	2978	2766

[a] TOT·2 was grown from 34% optically pure 2; the optical purity of guest in the measured crystal is estimated to be 70% (see text). [b] Grown from racemic 10. [c] Grown from optically pure material. [d] Densities were measured at room temperature; calculated densities are given for cell constants at room temperature. Calculated densities at −50 °C are as follows: 2, 1.209; 10,[b] 1.172; 10,[c] 1.172; 9,[c] 1.170. [e] The number of host molecules in the unit cell is given; in all cases the host:guest ratio is 2:1.

Table III. Atomic Coordinates (Standard Deviation) for *M*-(–)-TOT in TOT·(*R*,*R*)-(+)-9 (×10^4). Only Non-Hydrogen Atoms Are Included. Atom Numbering is Given in Figure 1

atom	*x*/*a*	*y*/*b*	*z*/*c*
O_1	3378 (3)	8130 (3)	1711 (1)
O_2	3295 (3)	9782 (3)	1066 (1)
O_3	4638 (3)	8775 (3)	937 (1)
O_{11}[a]	1613 (7)	6787 (6)	1510 (3)
O_{12}[a]	1828 (6)	6967 (6)	1298 (2)
O_{22}	2013 (3)	8869 (4)	527 (1)
O_{33}	3750 (4)	7126 (3)	560 (1)
C_3	3746 (3)	6821 (3)	2106 (1)
C_4	4160 (3)	6052 (3)	2119 (1)
C_5	4556 (3)	5797 (3)	1735 (1)
C_6	4538 (3)	6309 (3)	1339 (1)
C_1	4124 (3)	7078 (3)	1326 (1)
C_2	3728 (3)	7333 (3)	1710 (1)
C_7	5017 (6)	6024 (6)	929 (2)
C_8	3305 (5)	7093 (5)	2535 (1)
C_9	2325 (6)	5999 (6)	2735 (2)
C_{10}	4270 (6)	7710 (6)	2866 (2)
C_{11}	2307 (4)	7792 (4)	1565 (2)
C_{14}	2202 (3)	10514 (2)	1432 (1)
C_{15}	1461 (3)	10418 (2)	1772 (1)
C_{16}	989 (3)	9455 (2)	2045 (1)
C_{17}	1259 (3)	8588 (2)	1979 (1)
C_{12}	2000 (3)	8684 (2)	1640 (1)
C_{13}	2471 (3)	9646 (2)	1366 (1)
C_{18}	694 (5)	7526 (5)	2271 (2)
C_{19}	2687 (5)	11549 (5)	1119 (2)
C_{20}	3244 (6)	12689 (5)	1376 (2)
C_{21}	1739 (6)	11464 (6)	815 (2)
C_{22}	2979 (2)	9356 (4)	650 (1)
C_{25}	5877 (2)	9775 (3)	327 (1)
C_{26}	6115 (2)	10448 (3)	–49 (1)
C_{27}	5310 (2)	10730 (3)	–206 (1)
C_{28}	4268 (2)	10338 (4)	13 (1)
C_{23}	4030 (2)	9665 (3)	390 (1)
C_{24}	4835 (2)	9384 (3)	547 (1)
C_{29}	3429 (2)	10689 (6)	–154 (2)
C_{30}	6786 (5)	9502 (5)	506 (2)
C_{31}	7862 (5)	10605 (9)	651 (2)
C_{32}	7062 (8)	8816 (7)	181 (2)
C_{33}	4112 (4)	7618 (4)	899 (2)

[a] Occupancy for this atom is 0.5.

molecules (the atomic coordinates of TOT in *M*-(–)-TOT·(*R*,*R*)-**9** are given in Table III); six form a cylindrical wall that is approximately parallel to the *c* axis; one molecule is on top and one on the bottom (looking at the cage along the *c* axis; Figure 3). The cage is located on a crystallographic 2-fold axis, and there are three cages in each unit cell; the maximum number of guest molecules in the unit cell is therefore three, and the maximum guest:host ratio is 1:2.

TOT Configuration and Orientation. Cage Size Variation. Variations in TOT atomic coordinates from one structure to another are very small. They are mainly due to the overall displacements of the TOT molecules. When two structures are positioned so that their origins and axes overlap (i.e., coincidence of their C_2 and C_3 axes, respectively), a displacement (rotation and translation) is required to minimize the differences in the coordinates of corresponding TOT molecules. The maximum displacement between two structures is quite small, 0.35 Å (mean difference 0.14 Å). The remaining discrepancy in TOT coordinates, once these displacements have been effected, is due to conformational differences, but these contribute much less to the differences in coordinates (0.15-Å maximum difference between structures; mean difference 0.04 Å).

Another way to evaluate the differences from one structure to another is to follow the change in the volume of the cages. For this purpose, we have defined the volume accessible to guest,[21] using a van der Waals radius of 2 Å for guest atoms and the van der Waals radii from ref 22 for host atoms. These variations of accessible volume are presented in Table IV, where it can be seen that there is a definite correlation between guest and volume variations. The slight changes in TOT orientation provide a clathrate with a limited degree of cavity flexibility for adapting to different sized guests. Despite the absence of strong interactions such as hydrogen bonds between the TOT host molecules, the range of these variations is very restricted: structurally and chemically similar molecules that are slightly larger than those that form cage clathrates, e.g., 2,5-dimethyltetrahydrofuran, give rise to other types of adducts[7] or do not form complexes at all.

Table IV. Comparison of the Volume of the van der Waals (VDW) Envelope Accessible to Guest to the VDW Volumes of the Guest Molecules

	guest				
	2	10[a]	10[b]	10[c]	9[a]
VDW vol of guest, Å^3 [d]	104	99	99	99	90
VDW envelope of vol accessible to guest, Å^3 [d]	111[e]	102[e]	102[e]	102[e]	96[e]

[a] Optically pure material. [b] Major enantiomer in a crystal grown from racemic guest. [c] Minor enantiomer in a crystal grown from racemic guest. [d] Calculations were done on a grid of 0.3-Å side, volumes of the cubes surrounding grid points in the envelope being added to give its volume; for points on the limits of this envelope, a Monte Carlo method was used to determine the part of the associated cube actually inside the envelope. [e] Calculations were done by using TOT coordinates with the position of the disordered carbonyl oxygen giving the smallest envelope volume; use of the other position consistently gives a larger volume (by ca. 10 Å^3) but does not change significantly the overlaps of TOT and guest.

Guest Orientation. The shape of the cage resembles a deformed ellipsoid in which differences in axial lengths (Figure 4) prevent random orientation of guests. There is a complementarity of guest and cavity shape even though the cavity is relatively featureless and the guest molecules are disordered. All guests, both those with C_1 and those with C_2 molecular symmetry, were found to be disordered about the 2-fold axis. Interestingly, in order to best comply with crystalline symmetry, molecules such as 2-bromobutane (**2**) occupy two symmetry-related positions with the bromine atoms of the two symmetry-related positions lying near the 2-fold axis and the two methyl groups (Me-CHBr and Me-CH_2) of both orientations nearly overlapped (Figure 5a). Optically pure **9** and **10** are also disordered about the 2-fold axis; in these structures, due to the molecular symmetry, the CH groups nearly overlap, and the molecules are much closer to crystallographic special positions (Figure 5b).

The longest dimension of **9** and of **10** precludes orientations other than those observed in the structures. Thus, the methyl groups have the same positions in the cage for these molecules (see Table V). In Figure 4 it is clearly seen that the cage is flat on one side along the 2-fold axis and has a bulge on the other side where the oxygen and sulfur atoms of **9** and **10**, respectively, are accommodated.

Crystallographic Data on Guest Enantiomeric Disorder. In addition to the orientational disorder of the guests (that is, different orientations of a single enantiomer), disorder involving an inversion of absolute configuration has been observed in the clathrates studied here. 2-Bromobutane (**2**) may be configurationally inverted most simply by the exchange of methyl and bromine substitutents; we denote this disorder, where two ligands are exchanged but the remaining ligands on the chiral center(s) remain fixed, as "ligand-exchange" enantiomeric disorder (ligand-exchange disorder of the bromine and the hydrogen or of the methyl and hydrogen should not occur because of the differences in size. With a guest such as **11**, methylene–oxygen ligand-exchange disorder is also possible).

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(20) Brunie, S.; Navaza, A.; Tsoucaris, G.; Declercq, J. P.; Germain, G. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2645.

(21) Lee, B.; Richards, F. M. *J. Mol. Biol.* **1971**, *55*, 379.

(22) (a) Ramachandran, G. N.; Sasisekharan, V. *Adv. Protein Chem.* **1968**, *23*, 284. (b) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

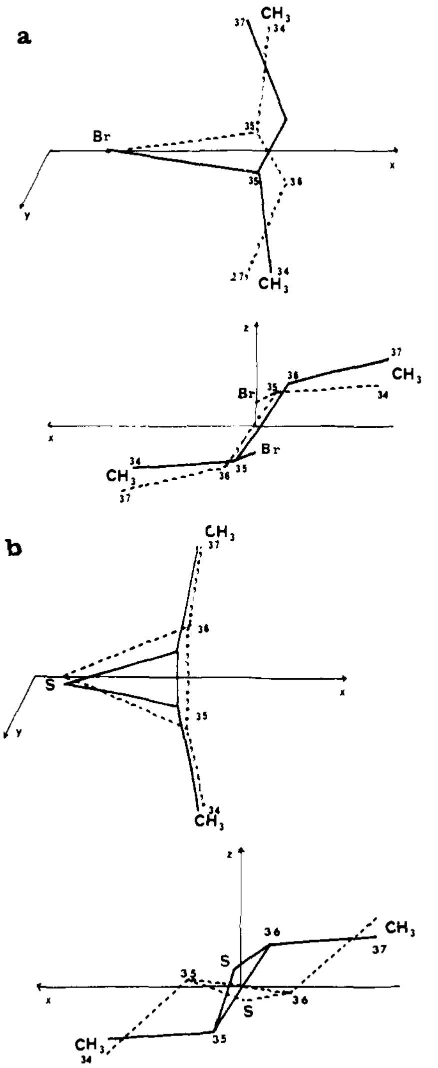

Figure 5. (a) Projections on the $x0y$ and the $x0z$ planes showing the two positions of the major enantiomer in the TOT clathrate which are related by a 2-fold axis. (b) Projections on the $x0y$ and the $x0z$ planes of the major (full line) and minor (dashed line) enantiomers of 2,3-dimethylthiirane in TOT·**10** grown from racemic material. This illustrates "mirror reflection" enantiomeric disorder.

Table V. Atomic Coordinates (Standard Deviations) of Guest Molecules Associated to *M*-(−)-TOT (×10^4)

atom[a]	x/a	y/b	z/c
	(*R*)-(−)-2-Bromobutane		
Br	14 (4)	2076 (3)	1791 (1)
C_{34}	−1483 (17)	2976 (22)	1860 (8)
C_{35}	−222 (18)	3384 (18)	1836 (8)
C_{36}	375 (18)	4180 (19)	1462 (9)
C_{37}	1549 (17)	4376 (21)	1345 (8)
	(*R*,*R*)-(+)-*trans*-2,3-Dimethylthiirane[b]		
S	72 (8)	2183 (5)	1735 (3)
C_{34}	1572 (8)	4429 (5)	1371 (3)
C_{35}	341 (8)	3473 (5)	1453 (3)
C_{36}	−400 (8)	3192 (5)	1848 (3)
C_{37}	−1658 (8)	2841 (5)	1898 (3)
	(*R*,*R*)-(+)-*trans*-2,3-Dimethyloxirane[b]		
O	129 (10)	2364 (6)	1724 (4)
C_{34}	−1501 (10)	2732 (6)	1926 (4)
C_{35}	−207 (10)	3143 (6)	1901 (4)
C_{36}	316 (10)	3341 (6)	1462 (4)
C_{37}	1591 (10)	4171 (6)	1371 (4)
	(*R*,*R*)-(+)-*trans*-2,3-Dimethylthiirane[c]		
S	107 (8)	2213 (6)	1801 (3)
C_{34}	1620 (8)	4444 (6)	1428 (3)
C_{35}	386 (8)	3491 (6)	1507 (3)
C_{36}	−369 (8)	3226 (6)	1897 (3)
C_{37}	−1629 (8)	2877 (6)	1937 (3)
	(*S*,*S*)-(−)-*trans*-2,3-Dimethylthiirane[d]		
S_2	−44 (26)	2120 (17)	1677 (9)
C_{34}	−1457 (28)	2877 (17)	2068 (9)
C_{35}	−640 (28)	3059 (17)	1682 (9)
C_{36}	617 (28)	3662 (17)	1680 (9)
C_{37}	1489 (27)	4283 (17)	1313 (9)

[a] For atom numbering, see Figure 1. [b] In the crystal grown from optically pure material. [c] Major enantiomer in the crystal grown from racemic material; enantiomers ratio in the crystal 2:1. [d] Minor enantiomer in the crystal grown from racemic material; enantiomers ratio in the crystal 2:1.

Another way for achieving enantiomeric disorder in **2** involves changing the butane chain pucker, in a fashion similar to that found for **9** and **10** (Figure 5b) and for *sec*-butyl groups in general.[15] In this type of disorder the enantiomers are related by a mirror plane that contains the long axis of the molecule and keeps the methyl and the bromine almost unchanged from their original positions, while inverting the absolute configuration of the asymmetric carbon. This second kind of enantiomeric disorder, which we denote as "mirror reflection" disorder, would be most likely with guests such as **9** or **10** (assuming, as is indeed observed, that the heteroatom lies in the C_2 axis bulge). Two questions may be raised: what kind of disorder is responsible for the presence of both enantiomers in a cage of a given chirality, and what are the interactions between the guest and the TOT that are responsible for the observed preference for one enantiomer?

In the case of TOT·**2**, only one enantiomer could be located on the electron density maps. The refined occupancy of this major enantiomer was 0.85, so that the minor enantiomer, having an occupancy of 0.15, should have been detectable. Spurious peaks in the difference synthesis at the completion of the structural refinement had a height of 0.3 e/Å^3, which is very small compared to the peak heights of the carbon atoms of the major guest enantiomer, 1.5 e/Å^3. The remaining density was located mainly on the 2-fold axis and near the bromine and methyl groups of the major guest enantiomer. An attempted assignment of these peaks to the bromine atom of the minor guest enantiomer was rejected when tentative refinement of the coordinates of this atom led either to a substantial increase of the R factor or to spurious peaks in difference maps.

In contrast to the case of TOT·**2**, the positions of both enantiomers could be readily identified in a TOT clathrate crystal grown from racemic **10**; the ratio of enantiomers was 2:1 (see Table I). The minor enantiomer was unambiguously located on a Fourier difference map after the major enantiomer was identified. Refinement without the minor enantiomer led to an increase of the R factor. The methyl and sulfur positions are only slightly modified in the two enantiomers, but there is significant change in the coordinates of the methine carbons (see Figure 5b and Table V).

Relation of Structural Data to Guest Enantiomeric Purity and Host–Guest Correlation of Configuration. The stereochemical data on the relative orientation and position of host and guest in various TOT clathrates can now be compared to the respective data on guest enantiomeric disorder, namely, the preference for one enantiomer in "ligand-exchange"-type disorder or in "mirror reflection" type disorder.

It might have been argued that the difference of the shapes of the two enantiomers of **2** obtained by bromine–methyl exchange would be sufficient to rule out the presence of the unobserved species. When short van der Waals contacts between **2** and host were minimized by varying the guest orientation, position, and internal degree of freedom (**2** was nevertheless kept near its lower energy conformation[23a]), it was found that the short contacts of both enantiomers of **2** could be minimized to a comparable extent (Table VI). The actual contacts of both enantiomers of **10** with

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(23) (a) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformation Analysis"; Wiley: New York, 1965. (b) Bernstein, J.; Hagler, A. T. *J. Am. Chem. Soc.* **1978**, *100*, 673.

Table VI. Contacts of 2-Bromobutane Enantiomers Obtained by Br-Me Exchange ("Ligand-Exchange"-Type Enantiomeric Disorder), after Minimization of Repulsive Contacts, with TOT Host Molecules[a]

obsd enantiomer		isomer obtained by Br-Me exchange	
atoms	dist (sum of VDW radii), Å	atoms	dist (sum of VDW radii), Å
$Br-H_{15}{}^{i}$	2.78 (2.85)	$Br-O_{11}{}^{v}$	3.44 (3.45)
$Br-C_{31}{}^{ii}$	3.78 (3.85)	$Br-C_{6}{}^{iv}$	3.58 (3.70)
$Br-H_{15}{}^{iii}$	2.78 (2.85)	$Br-C_{1}{}^{iv}$	3.66 (3.70)
$Br-C_{21}{}^{iii}$	3.84 (3.85)	$Br-C_{29}{}^{ix}$	3.76 (3.85)
$C_{34}-O_{11}{}^{iv}$	3.26 (3.40)	$C_{34}-H_{15}{}^{i}$	2.80 (2.95)
$C_{34}-C_{6}{}^{iv}$	3.64 (3.65)	$C_{34}-H_{15}{}^{iii}$	2.84 (2.95)
$C_{34}-C_{1}{}^{iv}$	3.63 (3.65)	$C_{34}-C_{29}{}^{vi}$	3.71 (3.80)
$C_{37}-C_{29}{}^{vi}$	3.77 (3.80)	$C_{37}-C_{6}{}^{v}$	3.52 (3.65)
$C_{37}-O_{11}{}^{v}$	3.30 (3.40)		

[a] Atom numbering given in Figure 1. Symmetry codes defining the host molecule atom in contact with guest are given in Table VII. Subscripts refer to atom numbers; superscripts refer to symmetry codes.

Table VII. Contacts of Major and Minor Enantiomers of **10** ("Mirror Reflection" Enantiomeric Disorder) with TOT Host Molecules

atom in guest-atom in TOT[a]	dist (sum of VDW radii), Å	atom in guest-atom in TOT[a]	dist (sum of VDW radii), Å
2,3-Dimethylthiirane Major Enantiomer[b]			
$S-H_{15}{}^{i}$	2.72 (2.85)	$C_{37}-C_{4}{}^{v}$	3.69 (3.70)
$S-C_{31}{}^{ii}$	3.79 (3.85)	$C_{37}-C_{5}{}^{v}$	3.57 (3.70)
$C_{34}-O_{11}{}^{iv}$	3.25 (3.35)	$C_{37}-C_{6}{}^{v}$	3.47 (3.70)
$C_{34}-C_{5}{}^{iv}$	3.62 (3.70)	$C_{37}-C_{1}{}^{v}$	3.51 (3.70)
$C_{34}-C_{6}{}^{iv}$	3.54 (3.70)	$C_{37}-C_{2}{}^{v}$	3.63 (3.70)
$C_{34}-C_{1}{}^{iv}$	3.59 (3.70)	$C_{37}-C_{20}{}^{i}$	3.98 (4.00)
$C_{34}-C_{20}{}^{viii}$	3.95 (4.00)	$C_{37}-O_{12}{}^{v}$	3.35 (3.35)
$C_{34}-C_{29}{}^{vi}$	3.98 (4.00)	$C_{35}-C_{29}{}^{vi}$	3.03 (3.20)
$C_{37}-O_{11}{}^{v}$	3.19 (3.35)		
2,3-Dimethylthiirane Minor Enantiomer[c]			
$S-C_{21}{}^{i}$	3.99 (4.00)	$C_{34}-C_{1}{}^{iv}$	3.66 (3.70)
$S-C_{31}{}^{ii}$	3.90 (4.00)	$C_{34}-C_{20}{}^{viii}$	3.86 (4.00)
$S-H_{15}{}^{i}$	2.81 (2.85)	$C_{37}-C_{6}{}^{v}$	3.58 (3.70)
$C_{34}-C_{29}{}^{vi}$	3.78 (4.00)	$C_{37}-C_{1}{}^{v}$	3.66 (3.70)
$C_{34}-C_{5}{}^{iv}$	3.69 (3.70)	$C_{37}-C_{20}{}^{viii}$	3.87 (4.00)
$C_{34}-C_{6}{}^{iv}$	3.57 (3.70)	$C_{37}-C_{29}{}^{vi}$	3.59 (4.00)

[a] Atom numbering given in Figure 1. Symmetry codes defining the atom of host in contact with guest are as follows: *i*, $x, y-1, z$; *ii*, $-x+1, y-x, +{}^{1}/_{3}-z$; *iii*, $-x, y-x-1, {}^{1}/_{3}-z$; *iv*, $-x, y-x, {}^{1}/_{3}-z$; *v*, x, y, z; *vi*, $y-1, x, -z$; *vii*, $-x+1, x+y+1, z+{}^{1}/_{3}$; *viii*, $-x, y-x-1, {}^{1}/_{3}-z$; *ix*, $-y+1, x-y+1, {}^{3}/_{3}+z$. Operations of symmetry are given for crystals of space group $P3_121$, i.e., including (*R*,*R*)-(+)-10 or (*R*)-(−)-2. [b] Major enantiomer in the crystal grown from racemic material; ratio of enantiomers estimated by VPC analysis[10] 2:1. The mean standard deviation of the contact distances is 0.03 Å. [c] Minor enantiomer in the crystal grown from racemic material; ratio of enantiomers estimated by VPC analysis[10] 2:1. The mean standard deviation of the contact distances is 0.05 Å.

the cage are also very comparable (Table VII). Therefore, the observed enantiomeric preference, whether in "ligand-exchange"-type disorder or in "mirror reflection"-type disorder, can be attributed not to any predominant interaction of one guest atom with the host but to the contribution of all such interactions. The necessity of using an entire set of atom–atom potentials to account for the energy difference between two crystal forms has been demonstrated elsewhere.[23b]

Although one cannot point out specific host–guest interactions that would account for the observed discrimination,[24a] the determined structures suggest that the kind of disorder that prevents more efficient chiral discrimination from being observed involves the guest atoms located at the center of the cage; chiral discrimination is expected to improve when that disorder is hindered. Ways to achieve that seem to be indicated by inspection of the crystal structures which have been solved. On one hand, improved chiral discrimination is seen to be correlated either to a smaller volume of the cage (**9** compared to **10**) or to a bulkier substituent (located in the center of the cage) near the chiral center (**17**[24b] compared to **15**, assuming similar crystal structures for the two on the basis of identical absolute configuration correlations and the known stereochemistry of **15**). On the other hand, for a larger heteroatom substituent located at the edge of the cage near the chiral center (**2** or **10** compared to **9**) there is an increase of the size of the cage and also a decrease in chiral discrimination.

Sulfinate Racemization within the Cavity of the Cage. It was of interest to see whether the cage cavity expresses any chiral influence on a reaction in the crystals beyond that shown during the crystallization. Of the guests examined herein, methyl methanesulfinate, **15**, has a sufficiently low barrier to enantiomerization and is sufficiently stable to thermal rearrangement that one could study the influence of TOT enclathration on that barrier and on the enantiomer distribution when the barrier is overcome in the crystal.

Single crystals of TOT·**15**, which, like the other TOT cage complexes, do not have a sharp melting point and melt at 175–185 °C, were heated at various temperatures, and the guest enantiomeric excess was determined. It was done by dissolving the crystal in $CDCl_3$ containing the chiral shift reagent $Eu(dcm)_3$[25] and integrating the $S-CH_3$ signals of the *R* and *S* enantiomers. No change in the ee (14%, Table I) was observed in crystals that were heated at 115 °C for up to 12 h; in solution, complete racemization was observed under these conditions. However, on heating the crystals at 125 °C for 12 h, racemization proceeded and the ee fell to zero. Powder photography before and after the heating indicated that the integrity of the cage clathrate structure has not been destroyed, and it is therefore likely to assume that enantiomerization takes place within the TOT cage cavities which afford appreciable stabilization of **15** toward racemization.

These observations may be ascribed to the flexibility of the TOT molecule.[5] When sufficient thermal energy is introduced, the motion of the TOT molecules and the expanded cage allow enantiomerization of the guest; the thermally excited cavity no longer shows any chiral discrimination, and the guest ee falls to zero. On cooling, the racemization barrier of the guest is apparently passed before the TOT cavity returns to a state where chiral discrimination is expressed.

Preparative Resolution Using TOT. Since large (1 g) single crystals of TOT clathrates can generally be grown,[17] preparative resolution is possible and of interest, especially with guests that are not resolvable by other procedures. One approach is to grow batches of large single crystals, separate the *P*-(+)- and *M*-(−)-TOT crystals (using a small chip of each crystal to determine its sign) and then to isolate enantiomerically enriched guest from each fraction. We followed this procedure with 2-bromobutane (**2**) and obtained from ten (+)-TOT·**2** crystals, total weight ~2.3 g, 200 μL (0.25 g) of 37% enantiomerically enriched (*S*)-(+)-2-bromobutane.

Since the growing of large single crystals is time consuming and tedious, we also used a different seeding technique. As an example of this approach, a single crystal of (−)-TOT·(*R*)-(−)-**2** was powdered and added to a saturated solution of TOT in racemic **2**; the polycrystalline clathrate that deposited on cooling contained **2** having an enantiomeric purity of ca. 85% of that in a single crystal. This method is relatively rapid and straightforward for obtaining an enantiomerically enriched sample of a desired guest.

Finally, the enantiomeric purity of the extracted, partially resolved guest, or of a nonracemic sample obtained by some other method, can be appreciably enhanced by a second, or repeated, enclathration in TOT. For channel-type clathrates there may be unexpectedly large enhancements of enantiomeric purity. This

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(24) (a) Packing energy calculations have recently been performed in order to account for the observed chiral discrimination. For a preliminary communication see: Gerdil, R.; Allemand, J. *Helv. Chim. Acta* **1980**, *63*, 1750. (b) Gerdil, R., personal communication.

(25) McCreary, M. D.; Lewis, D. W.; Wernick, D. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 1038.

is illustrated in Table IX for the case of 2-bromooctane.[26] For cage-type clathrates, the enhancement is essentially that expected on the basis of the intrinsic chiral discrimination (guest ee in single crystals when TOT is crystallized from racemic guest) and the enantiomeric purity of the starting solution. Differences in behavior of enantiomerically enriched and racemic solutions have been noted in other systems as well.[27] A possible explanation in the present example may be that as the clathrate crystal grows, guest–guest interactions that are present in the channel-type clathrates but are absent in the cage-type clathrates[28] cooperatively enhance the enantiomeric purity in the growing clathrate crystal.

Conclusion

Following our initial results on chiral discrimination in TOT clathrates,[29] we have presented here data on the scope of the possible resolutions. It is suggested that TOT clathrates may be useful for preparative resolutions of chiral molecules that cannot otherwise be separated and for the determination of absolute configurations.

The observed enantiomeric excess for various guest molecules, combined with the crystallographic data, led us to interpret the chiral discrimination in TOT cage clathrates as due to the overall dimensions (shape) of the cavity and not to specific points of contact between the guest and the walls of the cage. The relatively efficient resolution of *trans*-2,3-dimethyloxirane (**9**) and 2-bromobutane (**2**) demonstrates that the presence of hydrogen-bonding functional groups in the guest is not a prerequisite. The coincidence of guest and cavity symmetry appears to favor better discrimination in the series of guests studied.

The discriminating properties of the TOT cage cavity seem contradictory. Cages can accommodate highly polar molecules such as acids and alcohols yet also such apolar species as halocarbons and ethers. Despite this lack of specificity, it is seen that for all of the guest molecules having the general formula $CH_3X(Y)ZCH_3$ (for which crystal data are available), the methyl groups occupy nearly identical positions in the ellipsoid-like, 2-fold symmetrical cavity, there is no methyl–bromine disorder in the TOT·**2** clathrate, and relatively high (2:1) enantiomeric discrimination is possible.

The rationalization of chiral discrimination invariably involves models that are based on specific chemical interactions.[30-32] Although such stereochemical models have been important and useful, the exceptions that exist for nearly all of these models[31,33,34] demonstrate the limitations of a simplified view involving only a few specific chemical interactions as the sources of chiral discrimination. The TOT cage clathrate cavity suggests a different model, one in which the sum of many weak, nonspecific interactions provides chiral discrimination. The "model" aspects in the TOT cage are difficult to apply because in spite of the precise structural information, one cannot as yet predict the degree or direction of enantiomeric preference. The situation in the TOT clathrates is thus similar to that in enzymes where a fully resolved X-ray structure is insufficient to enable one to deduce substrate or function.[35]

Experimental Section

General Procedures. X-ray powder diffraction data were collected on a Philips powder diffractometer, using Cu Kα radiation. Crystal cell constants were measured from Weissenberg and rotation photographs or on a Nonius CAD-4 diffractometer using Cu Kα radiation. Optical rotations were measured on a Perkin-Elmer 141 polarimeter at 5890 Å using a 1-mL 10-cm path length cell. For low-temperature measurements, the cell was cooled to 1–2 °C by circulating ice-cooled water; a stream of dry nitrogen was passed over the cell windows to prevent condensation of moisture. In order to measure the rotations of solutions prepared from crystalline TOT clathrates, the samples (generally single crystals or portions thereof) were placed in 1-mL volumetric flasks and cooled to −10 °C or lower (ice–salt bath). Previously cooled chloroform was added, and after the crystal was dissolved at this temperature, the solution was transferred to the cooled polarimetric cell. Polarimetric measurements on very small samples were made in a micro cell, 60- or 100-μL volume, 10-cm path length, at 6328 Å using a He–Ne laser. VPC analysis of enantiomeric trifluoroacetylamines was performed on a Varian Aerograph 1200 instrument using 400-ft long, 0.02-in. i.d. stainless steel capillary columns coated with L-valine isopropyl ester ureide[36] or with *N*-lauroyl-(*R*)-α-(1-naphthyl)ethylamine.[11] Peak areas were estimated with a Spectraphysics minigrator or by the cut-and-weigh method. Other VPC analyses were performed on a Varian Aerograph 1200 instrument using a 6 ft × 1/8 in. column containing 10% SE-30 on chromosorb W30/60.

Starting Materials. Tri-*o*-thymotide (TOT) was synthesized from *o*-thymotic acid by treatment with $POCl_3$ in boiling xylene[3a] and purified by chromatography on silica gel. Final purification was achieved by crystallization from chloroform–cyclohexane. Solvent-free material was obtained by warming the crystals to 130 °C (0.2 mmHg) for 24 h. 2-Bromobutane (**2**; Fluka, purum), 2-chlorobutane (**1**; BDH), 2-iodobutane (**3**; BDH), 2-bromooctane (**5**; Eastman Kodak), 2-bromononane (**7**; K and K), 2-bromododecane (**8**; Aldrich), propylene oxide (**13**; Merck), *trans*-2,3-dimethyloxirane (**9**; Merck), and 2-methyltetrahydrofuran (**14**; Merck) were all commercial samples. *trans*-2,3-Dimethylthiirane (**10**) was synthesized from *trans*-2,3-dimethyloxirane (**9**) by using the thiourea method.[37] 2,4-Dimethyloxetane (**11**)[38] and 2,4-dimethylthietane (**12**) were synthesized from 2,4-pentanediol.[39] 2,3,3-Trimethyloxaziridine (**16**) was prepared from *N*-methylisopropylidenimine by oxidation with *m*-chloroperbenzoic acid;[40] it displayed *m/e* 87 (70 eV) and NMR ($CDCl_3$) δ 2.71 (s, 3 H, CH_3-N), 1.53 (s, 3 H, CH_3C), and 1.41 (s, 3 H, CH_3C). Methyl methanesulfinate (**15**) was prepared by adding methanol to methanesulfinyl chloride;[41] the latter was obtained from the reaction of methyl disulfide with acetic anhydride.[42] Optically active (*R*)-(−)-2-bromooctane was synthesized from (*S*)-(+)-2-octanol (Aldrich) by treatment with phosphorus tribromide[43] and had $[\alpha]_D$ −32.6° (neat liquid). Optically pure (*S*,*S*)-(−)-2,3-dimethyloxirane was synthesized from (*S*,*S*)-(+)-2,3-butanediol,[44] which was obtained enantiomerically pure from (*R*,*R*)-(+)-tartaric acid.[45] Enantiomerically enriched (*R*,*R*)-(+)-2,3-dimethylthiirane was synthesized from (*S*,*S*)-(+)-2,3-butanediol.[45] All known compounds had NMR spectra identical with those previously reported in the literature.

Single crystals of the clathrates were grown in two stages. Crystals weighing up to ca. 1 mg were obtained by slow cooling of hot, filtered, saturated solutions of TOT in the neat guest. Selected crystals were then used as seeds to grow larger single crystals. Details of the crystallization procedure and crystal data for each guest are summarized in Table VIII.

Enantiomeric Excess of Guest in Clathrate Crystals and Correlation of Host and Guest Configuration. Estimations of enantiomeric excess and host–guest configuration correlations were performed by VPC analysis, polarimetrically, and/or by NMR. Single crystals weighing from 8 to 200 mg were used, and the guest was isolated from one single crystal or from several crystals having the same absolute configuration. In order to rule out the effect of chiral impurities, single clathrate crystals having + and others having − sign for the TOT rotation were studied for each guest. The host optical rotation sign (and hence the absolute configuration of TOT in each crystal)[9] was determined by cutting a chip (1–2 mg) from the studied crystal and measuring its initial rotation at low temperature (1–2 °C). The initial rotation for a 1–2-mg sample was 0.1°. The enantiomeric excess and configuration of the dominant guest

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Table VIII. Crystal Data and Details for Growth of TOT Clathrates

guest[a]	concn of starting soln, mg of TOT/mL of guest	temp range for cryst growth, °C	space group[b]	$a = b$, Å	c, Å	d_c[c]	d_m	host:guest ratio
1	45	40, 0	$P3_121$	13.690 (2)	30.520 (2)	1.161	1.156	2:1
2	90	50, 0	$P3_121$	13.757 (8)	30.329 (8)	1.194	1.191	2:1
3	250	45, 25	$P3_121$	13.683 (5)	30.530 (3)	1.264	1.170	1:1
4	125	75, 0	$P6_1$	14.372 (9)	28.920 (2)	1.122	1.124	2.6:1
5	125	80, 0	$P6_1$	14.427 (2)	28.870 (2)	1.151	1.148	2.6:1
6	125	60, 0	$P6_1$	14.440 (1)	28.980 (3)	1.151		*d*
7	80	90, −20	$P3_1$	14.366 (2)	28.874 (7)	1.157	1.150	3:1
8	70	100, −20	$P6_1$	14.386 (4)	28.930 (2)	1.143	1.143	3.8:1
9	50	45, 0	$P3_121$	13.535 (3)	30.515 (8)	1.157	1.154	2:1
10	100	60, 0	$P3_121$	13.646 (3)	30.420 (1)	1.161	1.158	2:1
11	120	75, 25	$P3_121$	13.562 (3)	30.540 (1)	1.147	1.150	2:1
12	135	60, 0	$P3_121$	13.679 (3)	31.070 (2)	1.150	1.144	2:1
13	50	45, 0	$P3_121$	13.435 (2)	30.310 (2)	1.170	1.168	2:1
14	100	50, 0	$P3_121$	13.643 (2)	30.620 (1)	1.151	1.141	2:1
15	50	90, 25	$P3_121$	13.522 (3)	30.480 (1)	1.187	1.184	2:1
16	60	30, −20	$P3_121$[e]					2:1[f]

[a] Numbers as in Table I. [b] Space group is $P3_121$ or $P3_221$ and $P6_1$ or $P6_5$ ($P3_1$ or $P3_2$); the ambiguity can be removed by the knowledge of the absolute configuration of guest or host. [c] For full occupancy defined as two hosts to one guest in cage-type complexes and by taking into account the length of guest and the length of c axis in channel-type adducts. [d] See footnote 47. [e] From comparison to powder pictures of cage-type clathrates. [f] From NMR.

was determined as described below. These data are summarized in Table I.

2-Bromobutane (2). Ten crystals having a (+)-TOT rotation were chosen and used as seeds for further crystallizations. A total weight of 2.3 g of *P*-(+)-TOT·**2** was obtained. The bromobutane was extracted from the crystals by bulb-to-bulb distillation (180 °C, 0.5 mmHg, liquid nitrogen cooling of receiving bulb), and it was shown (VPC) that all of the guest was transferred from one bulb to the other, while the host (TOT) remained in the first one. The optical rotation of the guest (about 200 μL) was measured on a Perkin-Elmer 241 automatic polarimeter in a 100-μL, 1-cm path length cell, using Na 5890-Å radiation. The observed rotation (+1.41°) corresponds to $[\alpha]_D$ 11.2°. The corresponding enantiomeric excess and configuration of the major enantiomer are deduced from the $[\alpha]_D$ of (*S*)-2-bromobutane: +34°.[46]

2-Chlorobutane (1). The guest was extracted as described above for 2-bromobutane from a 250-mg crystal of (+)-TOT·**1**. The guest (10 μL) was dissolved in 70 μL of chloroform, and the rotation of the solution was measured in a micropolarimeter at a wavelength of 6328 Å. The observed rotation was 1.197 ± 0.005°; the corresponding optical purity and absolute configuration were deduced from the $[\alpha]_D$ of (*S*)-2-chlorobutane: +37°.[46]

2-Bromooctane (5), 2-Chlorooctane (4), 3-Bromooctane[47] (6), 2-Bromononane (7), and 2-Bromododecane (8). Well-developed single crystals of TOT clathrate weighing from 8 to 50 mg were selected, and a chip (1–2 mg) was removed and used to measure the sign of the TOT optical rotation. The remaining crystal was placed at the bottom of a 20 cm × 8 mm glass tube having partial constrictions (to enable easy flame sealing) one-third from the top and one-third from the bottom. The tube was evacuated (ca. 0.1 mmHg) and flame sealed at the upper constriction. It was heated (oil bath at 170–180 °C) for 30 min while the top end of the tube was cooled with dry ice. The guest material condensed at the top of the tube, and the TOT melt remained at the bottom. The tube was opened below the bottom constriction, and the residue was examined by VPC to ensure that all guest had been driven off. (In all cases less than 10% of guest was left behind; in experiments where conditions were deliberately chosen so that 10% of the guest remained with the TOT, the measured enantiomer excess was no different from that of a sample where 99% of guest had been removed.) Next, a 10-fold molar excess of ethanolic ammonia (ca. 0.1–0.3 mL) was added to the guest, and the tube was flame sealed at the remaining constriction. The sample was warmed for 12 h at 100 °C and opened, and the excess ethanolic ammonia was evaporated in a stream of air. Finally, the resulting 2-aminoalkane was dissolved in ca. 50 μL of acetone and cooled in liquid nitrogen, and a 10-fold excess of trifluoracetic anhydride was added; the solution, capped with a $CaCl_2$ tube, was allowed to warm to room temperature. Direct injection onto a capillary column coated with a chiral support provided the ratio of enantiomers by their relative peak areas. The samples were injected under conditions[11,36] that generally gave base line separation between the peaks of enantiomers. The conditions are (column temperature, He flow) for the ureide column: 125–135 °C, 4.5 mL/min and for the *N*-lauroyl-(*R*)-α-(1-naphthyl)ethylamine column: 120–140 °C, 4.5 mL/min. When the two enantiomeric peaks were not base line separated, the ratio was estimated by comparison to a racemic material injected under the same conditions. The absolute configuration of the major guest enantiomer was determined by comparison with an authentic enantiomerically enriched sample (for *N*-TFA-2-aminooctane) or by analogy to previously studied materials.[36]

Propylene Oxide (13), 2,3-Dimethyloxirane (9), 2,3-Dimethylthiirane (10), 2,4-Dimethyloxetane (11), and 2,4-Dimethylthietane (12). Crystals weighing from 15 to 50 mg were prepared, and a chip was removed from each of them for measurement of the sign of rotation of the TOT. The remaining part was placed in a septum-capped 5-mL vial and was melted by heating to 180 °C. A few microliters of the guest's vapor was then injected onto a capillary column, coated with a chiral support.[10,45] The ratio of enantiomers was estimated by the cut-and-weigh method and by integration; in all cases base line separation was obtained. For guests **9**, **10**, and **13**, the absolute configuration of the major guest enantiomer was determined by comparison with authentic, enantiomerically pure material.

2-Methyltetrahydrofuran (14). A large single crystal of TOT·**14** (140 mg) was powdered and added at 45 °C to 10 mL of a saturated solution of TOT in racemic **14**. After continuous stirring for 3 days at 4 °C the solution was cooled to −20 °C and stirred for an additional 3 days; 670 mg of TOT·**14** were isolated, 20 mg of which were used to determine the sign of TOT rotation. The guest, extracted from the remaining crystals (40 μL), was diluted in chloroform (60 μL), and its rotation was measured by using the He–Ne laser polarimeter. The absolute configuration of the dominant guest was obtained by comparing the measured rotation ($[\alpha]_D$ −0.160 ± 0.005°) to that of neat (*R*)-**14**[48] at the Na line.

Methyl Methanesulfinate (15). The enantiomeric excess was determined by NMR using the chiral shift reagent $Eu(dcm)_3$. The correlation of major guest's and TOT configurations was made on a 50-mg clathrate crystal. A chip was used to determine the sign of the TOT rotation, and the remaining crystal was dissolved in 200 μL of CD_2Cl_2. The final optical rotation after complete racemization of TOT was measured with the He–Ne laser and was found to be $[\alpha]_D$ −0.16°. Comparison was made with other alkyl sulfinates,[49] all of which have (−) rotation for the (*R*)-absolute configuration.

2,3,3-Trimethyloxaziridine (16). The ee was determined by using NMR with a 1:1 ratio of $Eu(dcm)_3$ in $CDCl_3$ at −8 °C. Under these conditions the $N{-}CH_3$ signal, originally at δ 2.71, appeared as two lines

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Table IX. Optical Purity Enhancement on Crystallization from Optically Active **5**

enantiomeric purity in starting soln, %	0	12	35	50
enantiomer ratio in starting soln	50:50	56:44	67:33	75:25
expected enantiomer ratio in crystals[a]		58:42	69:31	77:23
enantiomeric purity in resulting crystals,[b] %	5[c]	30	66	80
obsd enantiomer ratio in crystal	53:47	65:35	83:17	90:10

[a] Calculated from the "intrinsic" chiral discrimination (52.5/47.5) × (the enantiomeric ratio in the starting solution), with the product normalized to a total numerator + denominator = 100; e.g., for 12% initial optical purity, (56/44) × (52.5/47.5) = 58.5/41.5, a 17% enantiomeric excess. [b] Maximum error limit, ±10% of value. [c] Single crystals.

at δ 3.05 and 3.26. Single crystals of the clathrate (20–30 mg) were dissolved in $CDCl_3$ (0.5 mL), and before the chiral shift reagent was added, the volatile guest and solvent were flash evaporated into an NMR tube in order to avoid overlap of TOT and **16** NMR signals.

Attempted Growth of *M*-(−)-TOT·(*S*,*S*)-(−)-9 Clathrate. In a typical experiment, TOT (14 mg) was dissolved in hot (*S*,*S*)-(−)-**9** (0.4 mL) and cooled to room temperature; a nearly saturated solution resulted. A seed crystal (15 mg) grown from (*R*,*R*)-(+)-**10** was suspended in the solution, which was slowly cooled to 4 °C. The seed crystal, which had decreased in size, comprised (−)-TOT; polycrystalline clathrate that had deposited at the bottom of the vessel comprised (+)-TOT. Repeated attempts led to the same result although seeds of TOT·**10** grew well in TOT solutions of (±)-**9**.

Resolution of a Large Amount of Material. Larger amounts of optically active **2** than those obtained from single crystals were conveniently obtained by a seeding method. Solvent-free TOT (5 g) was dissolved in racemic **2** (47 mL) at 45 °C, and the solution was filtered. Selected crystals of *M*-(−)-TOT clathrate containing an excess of (−)-**2** (495 mg) were powdered and added to the solution, which was cooled to 0 °C and stirred for 3 days and then cooled to −15 °C and stirred for another 3 days. The fine crystalline powder that was obtained (3.78 g) was filtered, washed with cold acetone, and dried. 2-Bromobutane (**2**; 300 μL) was distilled out of the crystals as described above. The optical rotation was measured in a 100-μL 1-cm cell and found to be $[\alpha]_D$ 9.5°; the $[\alpha]_D$ of extracted guest from a single clathrate cyrstal was 11.2°.

Amplification of Guest Optical Purity by Crystallization of Polycrystalline Clathrate from Optically Active Guest. Polycrystalline samples of TOT·**5** weighing ca. 20 mg were grown by slow cooling (from 80 to 0 °C) of solutions containing TOT (50 mg) in **5** (0.3 mL) that had varying enantiomeric excess. The solutions were obtained by mixing enantiomerically enriched and racemic **5**; the final optical purities were determined by converting a small sample (0.02 mL) to *N*-TFA-2-aminooctane and measuring the ratio of enantiomers as described above. Each batch of crystals was rinsed twice with acetone to avoid coating of the crystals with enantiomerically enriched solvent; the guest was extracted and analyzed. Values of the enantiomeric excess are given in Table IX.

Racemization of Methyl Methanesulfinate (15) in TOT Clathrates. Single crystals of TOT·**15** (20–50 mg) were dissolved in $CDCl_3$ (0.3 mL) containing tris(*d*,*d*-dicampholylmethanato)europium(III), 1:1 molar ratio of guest:chiral shift reagent, and the NMR spectra recorded between 0 and 10 °C. Under these conditions the *S*-CH_3 signal, originally at δ 2.62, was shifted to a lower field and split into two lines with base line separation of enantiomeric peaks; the *S*-OCH_3 signal, originally at δ 3.76, also shifted to lower field but was not clearly split under these conditions. To estimate the experimental error in the measurements, two halves of the same crystal were measured, and the values of enantiomer ratio were compared; they were different by less than 10% of the value. Single crystals (20 mg) were then heated overnight in sealed tubes, and the optical purity of the guest was measured; the results were as follows: temperature of heating (optical purity) 38 °C (13%), 115 °C (13%), 125 °C (0%). When a single crystal was dissolved in $CDCl_3$ and heated overnight to 115 °C in a sealed tube, the ee was 0%.

Crystallographic Studies on Cage-Type Clathrates. Four isomorphous crystal structures of TOT clathrates prepared from enantiomerically enriched (+)-**2**,[50] (±)-**10**, (*R*,*R*)-(+)-**9**, and (*S*,*S*)-(−)-**10** were determined. Preliminary data collected on films showed the crystals to belong to the trigonal space group, $P3_121$ (or $P3_221$). Accurate cell dimensions were determined at room temperature and −50 °C with an Enraf-Nonius CAD-4 diffractometer using Cu Kα radiation (λ 1.5418 Å). For each structure two data sets were collected at −50 °C, one for low θ ($\theta < 25°$) using a small crystal (less than 0.2 mm in each dimension) and a graphite monochromator, and a complete data set using a larger crystal and a nickel filter. Those two data sets were then scaled by using common reflections of medium intensity, and the final set of measurements was composed of the data from the small crystal for low θ and of the larger crystal's reflections for high θ. The θ limit was chosen so that the percentage of weak reflections ($I < 2\sigma(I)$) in the outer shell of Ewald sphere was smaller than 30% of the total number of reflections in that shell. All data were collected with the ω–2θ scan technique, and three standard reflections measured after every 100 reflections indicated that no change occurred during data collection; continuous recording of temperature warranted its stability. Measurements were not corrected for absorption. Crystal data are summarized in Table II. All structures were refined starting from the previously determined TOT coordinates in the isomorphous TOT·pyridine clathrate.[6] Three reflections (0,1,2), (0,0,3), and (0,0,6), probably affected by secondary extinction, were suppressed from the refinement. After isotropic refinement of the TOT molecule, the guest, or part of it, was located on a Fourier difference map, and its coordinates were refined as described for each structure. After completion of the isotropic refinement, hydrogen atoms were introduced in calculated positions or refined as rigid methyl groups, using the SHELX program.[51] All ordered non-hydrogen TOT atoms were refined anisotropically. Atomic coordinates of TOT atoms are given in Table II. Atomic coordinates of guest molecules are in Table V. Details of each structure resolution are described below.

TOT·(+)-2. The bromine atom was refined anisotropically; all other guest atoms were then located on a difference map. Guest was restrained to its standard geometry and refined with isotropic temperature factors; it is disordered around the crystallographic 2-fold axis; bromine atom is located near that axis and is highly anisotropic. Guest occupancy factor was first estimated from peak heights on difference maps and from the expected optical purity of guest in the crystal; this was calculated from the enantiomeric purity of the solution from which the crystal was grown and the expected enhancement of enantiomeric purity through clathrate formation. An occupancy factor of 0.45 gave the best agreement of calculated and observed X-ray data and was kept fixed in the last cycles of refinement. Spurious peaks in difference maps after complete refinement were smaller than 0.25 carbon atom, and the minor enantiomer of **2** could not be located; its most noticeable atom is a bromine of 0.05 occupany factor, which is probably smeared in the noise. One carbonyl oxygen of TOT was found to be disordered, with an occupancy factor of 0.5 in each position. The final R_{obsd} factor is 7.6%. Hamilton's test[52] was used to substantiate the assignment of the absolute configuration of 2-bromobutane; an inversion of the asymmetric carbon configuration led to an increase of the R_{obsd} factor to 9.1%.

TOT·10. As the crystal was grown from racemic material, both enantiomers of guest coexist in the crystal; the sulfur atom of the major enantiomer was located on a difference map and refined anisotropically. Its occupancy (0.66) could be deduced from the measured enantiomeric purity of guest in TOT clathrate grown from racemic material (see above). The major enantiomer was then refined isotropically in its standard geometry, deduced from that of ethylene sulfide,[53] carbon atoms being given a common temperature factor. The minor enantiomer was subsequently refined in the same way. Refinement of sulfur atom of the major guest enantiomer revealed its high anisotropy. One carbonyl oxygen of TOT was found to be disordered in two positions. After completion of the refinement, spurious peaks on difference maps were lower than half-height of a carbon atom in the minor guest enantiomer (i.e., 0.15 carbon atom). The final R_{obsd} factor is 8.7%.

TOT·(*S*,*S*)-(−)-10. Optically pure guest was refined in its standard geometry, the sulfur atom being given an anisotropic temperature factor whereas the rest of the molecule was considered as isotropic. One carbonyl oxygen of the TOT molecule was found to be disordered, with an occupancy factor of 0.5 in each position. The other carbonyl oxygens and one of the isopropyl methyls had temperature factor higher than the average of other TOT atoms temperature factors, although no clear-cut

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J. Am. Chem. Soc. **1983,** *105,* 4571–4575 4571

disorder could be detected. The sulfur atom is highly anisotropic. The final R_{obsd} factor is 8.3%.

TOT·(*R*,*R*)-(+)-9. Crystal structure determination had the same characteristics as that of TOT·(*S*,*S*)-(−)-**10**; the final R_{obsd} factor is 6.4%.

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Supplementary Material Available: Atomic coordinates and thermal parameters in cage-type clathrates with 2-bromobutane, enantiomerically pure 2,3-dimethyloxirane, enantiomerically pure 2,3-dimethylthiirane, and 66% enantiomerically enriched 2,3-dimethylthiirane as guests, and observed and calculated structure factors for (−)TOT·(*R*,*R*)-(+)-2,3-dimethyloxirane (31 pages). Ordering information is given on any current masthead page.

Electronic Absorption and Emission Spectra of Binuclear Platinum(II) Complexes. Characterization of the Lowest Singlet and Triplet Excited States of $Pt_2(H_2P_2O_5)_4{}^{4-}$

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Abstract: The low-temperature electronic absorption and emission spectra of single crystals containing a binuclear platinum anion, $Pt_2(H_2P_2O_5)_4{}^{4-}$, have been measured and analyzed. Absorption systems in the 450- and 360-nm regions are attributable to transitions to dσ*pσ excited states ($^3A_{2u}$ and $^1A_{2u}$, respectively). The Pt–Pt stretching frequency in the $^3A_{2u}$ state (155 cm^{-1}) is much larger than that (110 cm^{-1}) in the ground state (the $^3A_{2u}$ absorption as well as the fluorescence ($^1A_{2u} \rightarrow {}^1A_{1g}$) and phosphorescence ($^3A_{2u} \rightarrow {}^1A_{1g}$) spectra exhibit Pt–Pt stretching progressions), which accords with the dσ*pσ description of the excited state. The Pt–Pt bond is calculated to contract by 0.21 Å in the $^3A_{2u}$ state (relative to the ground-state value of 2.92 Å). Measurements of the phosphorescence spectrum of $Ba_2Pt_2(H_2P_2O_5)_4$ at low temperatures (8–4.2 K) confirm that there are two emitting levels split by 40.9 cm^{-1} (origins at 476.55 and 477.48 nm are assigned to the E_u and A_{1u} spin–orbit components of $^3A_{2u}$).

Our previous studies of the electronic spectroscopy and photochemistry of binuclear d^8·d^8 complexes have centered mainly on rhodium(I) systems, whose lowest excited state ($^3A_{2u}$; $(d\sigma)^2(d\sigma^*)^1(p\sigma)^1$) possesses a relatively strong Rh–Rh bond.[1-3] If our description of the d^8·d^8 interaction is correct, then it should be possible to manipulate the photophysical and photochemical properties of these systems by appropriate variations in the metal–metal interactions. In this context we have found that the intensely luminescent[4] platinum(II) complex,[5] $Pt_2(H_2P_2O_5)_4{}^{4-}$, is a most attractive system for study.[6] The excited-state lifetime of the potassium salt of this complex, $K_4Pt_2(H_2P_2O_5)_4 \cdot 2H_2O$ (Pt–Pt = 2.922 Å),[5] has been measured over a wide temperature range by Fordyce, Brummer, and Crosby.[7] From the latter study the zero-field splitting of $^3A_{2u}$ was estimated to be 49 cm^{-1}.

We now have developed a detailed electronic structural picture of binuclear d^8·d^8 systems through high resolution absorption and emission spectroscopic studies of single crystals of $Ba_2Pt_2(H_2P_2O_5)_4$. We have observed two emitting levels in the $^3A_{2u}$ region, thereby verifying the most important aspect of the Fordyce–Brummer–Crosby analysis.[7] Furthermore, we have elucidated fully the nature of the Pt–Pt bonding and other key aspects of structure in the lowest excited states of $Pt_2(H_2P_2O_5)_4{}^{4-}$.

Experimental Section

Instrumentation. Absorption spectra were measured on a Cary 17 absorption spectrometer equipped with a Hamamatsu R955 photomultiplier tube. Emission spectra were measured as follows: Light from a Hanovia 200 W Hg/Xe arc lamp was wavelength selected with a Spex Minimate monochromator and modulated at 108 Hz with a PAR Model 125A light chopper before excitation of the sample; the emitted light was dispersed with a Spex 1780 0.5-m monochromator and detected with a Hamamatsu R955 PMT; the signal was amplified with a PAR Model 186A lock-in amplifier equipped with a PAR 181 current sensitive preamplifier and displayed on a chart recorder. An Andonian O-24 variable-temperature liquid-helium optical dewar was used to obtain spectra at low temperatures. The sample temperature was measured with a calibrated 500 Ω carbon–glass resistor imbedded in a brass block near the sample.

Sample Preparation. $\mathbf{K_4Pt_2(H_2P_2O_5)_4 \cdot 2H_2O}$. A crude green sample of $K_4Pt_2(H_2P_2O_5)_4 \cdot 2H_2O$ was prepared by the method of Sadler.[5] It was precipitated from water by the addition of methanol to yield a yellow microcrystalline material. Pure yellow single crystals of $K_4Pt_2(H_2P_2O_5)_4 \cdot 2H_2O$ were grown as follows: Freshly precipitated $K_4Pt_2(H_2P_2O_5)_4$ (1.5 g) was dried on a vacuum line and then dissolved in 40 mL of degassed H_2O added to the powder by bulb-to-bulb distillation. The water was then slowly distilled away from the compound over several days by connecting the sample flask to a flask immersed in salted ice at −2 °C. In this way crystals could be grown in the absence of oxygen.

This method would on occasion yield very large (5 × 5 × 1 mm) bright yellow crystals with optical properties consistent with a tetragonal space group. X-ray photographs were taken of several of these samples. They displayed the same space group and unit cell dimensions as those obtained by Sadler. The crystals were typically square slabs exhibiting the 001 face with 110, $\bar{1}10$, $1\bar{1}0$, and $\bar{1}\bar{1}0$ faces as edges. Occasionally, 2 × 1 × 1 mm rectangular blocks were obtained with 110 and 001 faces as the larger surfaces.

$\mathbf{Ba_2Pt_2(H_2P_2O_5)_4}$. Three tenths of a gram of the potassium salt was dissolved in 10 mL of H_2O. An aqueous solution (10 mL) containing 1.0 g of $Ba(ClO_4)_2$ was added to this solution. Large yellow-green plates formed after several hours. These crystals exhibited a two-symmetry-

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