

## Quaternary Tröger Bases as New Inclusion Hosts: the First X-Ray Structures of a Tröger Base and of a Dioxane Clathrate

Edwin Weber,<sup>\*a</sup> Ute Müller,<sup>a</sup> Detlev Worsch,<sup>a</sup> Fritz Vögtle,<sup>a</sup> Georg Will,<sup>b</sup> and Armin Kirfel<sup>\*b</sup>

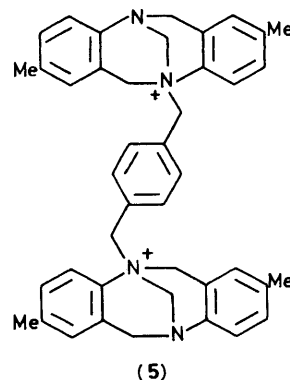
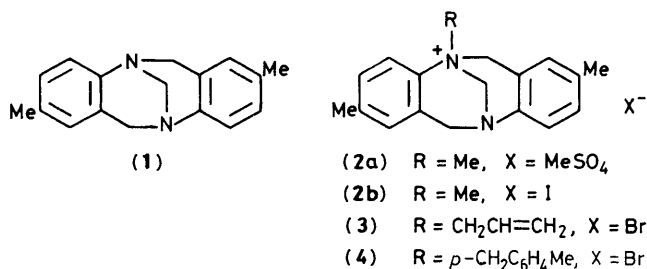
<sup>a</sup> Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Strasse 1, D-5300 Bonn-1, Federal Republic of Germany

<sup>b</sup> Mineralogisches Institut der Universität Bonn, Lehrstuhl für Mineralogie und Kristallographie, Poppelsdorfer Schloss, D-5300 Bonn-1, Federal Republic of Germany

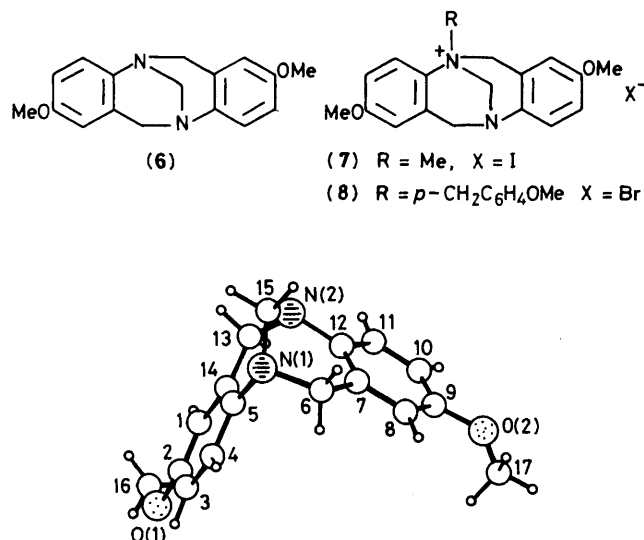
New clathrates of various onium salts (**2**)—(**5**), (**7**), and (**8**) of the Tröger bases (**1**) and (**6**) are described, including X-ray structures of the free host (**6**), and of an inclusion compound of (**2b**) with dioxane.

In the course of our search for new inclusion hosts<sup>1–3</sup> we became interested in an early note,<sup>4</sup> indicating purification problems with the crystals of the monomethylated Tröger base (**2a**), and hence entered into a series of hitherto unknown clathrate compounds. This is impressively shown by the various solvent inclusions of (**2a**).<sup>†</sup> Since the modified host compound (**2b**) has the same inclusion properties, the nature of the anion seems to have a bearing neither on the inclusion capacity of the quaternary Tröger base skeleton (**2**), nor on the stoichiometry of the clathrates formed. Additionally, the compounds (**3**)—(**5**), (**7**), and (**8**) have been synthesized in order to assess possible new inclusion selectivities effected by modified substituents.

The quaternary Tröger bases (**2**)—(**5**), (**7**), and (**8**) were synthesized by common alkylation methods (*cf.* ref. 4). No



<sup>†</sup> Inclusion compounds of stoichiometry 2:1 (host:guest) are formed by hosts (**2a**) or (**2b**) with guests: dioxane, benzene, toluene, ethylbenzene, chlorobenzene, *o*-, *m*-, *p*-xylene, 4-chlorotoluene, benzaldehyde, *D,L*-phenylethanol, cyclohexanone; 3:1 (host: guest) with mesitylene, acetophenone; 1:1 (host: guest) with benzyl alcohol; 3:2 (host: guest) with cyclohexanol. The following compounds could not be accommodated as guests: MeOH, EtOH, Bu<sup>o</sup>OH, Me<sub>2</sub>CO, CHCl<sub>3</sub>, cyclohexane, tetrahydrofuran, naphthalene, pyridine.



**Figure 1.** Perspective view of free dimethoxy Tröger base (6). Mean bond distances are C(sp<sup>3</sup>)-N 1.506, C(sp<sup>2</sup>)-N 1.447, C(sp<sup>3</sup>)-O 1.423, C(sp<sup>2</sup>)-O 1.373, C(sp<sup>2</sup>)-C(sp<sup>2</sup>) 1.381 Å.

bis-quaternization products of the Tröger bases (1) and (6) are observed under these conditions, even with use of excess of iodomethane, dimethyl sulphate, allyl halide, or benzyl halide, respectively, for alkylation.‡

As a general outcome of the clathrate study we find firstly that all investigated quaternary Tröger bases show inclusion properties, and secondly that they display a remarkable preference for aromatic guest solvents.† The allylic substituted Tröger base (3) exhibits an inclusion behaviour (clathrate stoichiometry included) very similar to the corresponding methyl derivatives (2a) or (2b). The inclusion selectivity of the *p*-methylbenzylated Tröger base (4), however, differs considerably from the above mentioned hosts. Less voluminous guest molecules, including acetone, Bu<sup>n</sup>OH, EtOH, but not MeOH (owing to the larger spatial demand of the *p*-methylbenzyl group), are now preferred in crystal lattice incorporation. The clathrate stoichiometries are also affected, being exclusively of 1 : 1 ratio in the case of (4) [in contrast to (2a, b)†]. The bis-Tröger salt (5) follows (4) in its inclusion selectivity and 1 : 1 clathrate stoichiometry. The quaternary derivatives (7) and (8) of Tröger base (6) largely correspond in their inclusion behaviour with the analogous salts of (1).

In order to investigate the inclusion selectivity with respect to different guest compounds, (2a) was recrystallized from 1 : 1 mixtures of those solvents with which it forms clathrates. The main results of these competition experiments are: dioxane is selectively incorporated into crystals of (2a) from mixtures with benzene or toluene; benzene being preferred over toluene, and toluene being favoured over xylenes.

In view of our general interest in the host-guest interaction and in the structural build-up of these new inclusion compounds, we have attempted *X*-ray structure analyses of the clathrates and of the free bases alone, since no crystal structure of a free Tröger base or of a quaternary salt of it has been reported yet.§

‡ Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds.

§ This is a surprising fact considering the stereochemical importance of the system, but is probably due to the poor quality of the crystals.

With respect to the free bases, only (6) was obtained as single crystals suitable for *X*-ray diffractometry.¶ Figure 1 depicts the molecular structure of (6). Thus, the *X*-ray structure analysis shows the skeleton of Tröger's base to exist in a conformation in which the benzene rings are nearly perpendicular to each other (91.1°), giving rise to a roof-like appearance of the molecule which seems favourable for inclusion behaviour.<sup>6</sup>

From the inclusion compounds, (2b)·0.5 dioxane was chosen for an *X*-ray structure analysis.¶ The packing scheme in the crystal of this compound is shown in Figure 2 which clearly reveals clathrate type of inclusion.<sup>7</sup> The dioxane atoms are free of any significant interaction, except dispersion forces, with the host environment, the iodide ions included (mean I-O 4.25 Å). Dioxane guests are embedded into quasi-channels of the host matrix. With one quaternary Tröger base molecule, one iodide ion, and one half of the dioxane molecule in the asymmetric unit, the dioxane possesses both a chemical and a crystallographic inversion centre, the latter giving rise to alternating layers of Tröger base molecules and iodide anions. The host molecule layers are composed of pairs of quaternary Tröger base individuals, each pair providing the void for the inclusion of the guest. While the vertical direction in Figure 2 is characterized by the close stacking of hosts, the horizontal direction indicates a polar region which accommodates the anions. Thus, the whole crystal is composed of alternating lamellar regions of opposite polarity. The dioxane molecules are found in the apolar regions, and the principal dioxane plane is tilted against the two principal host planes by 47 and 62°, respectively.

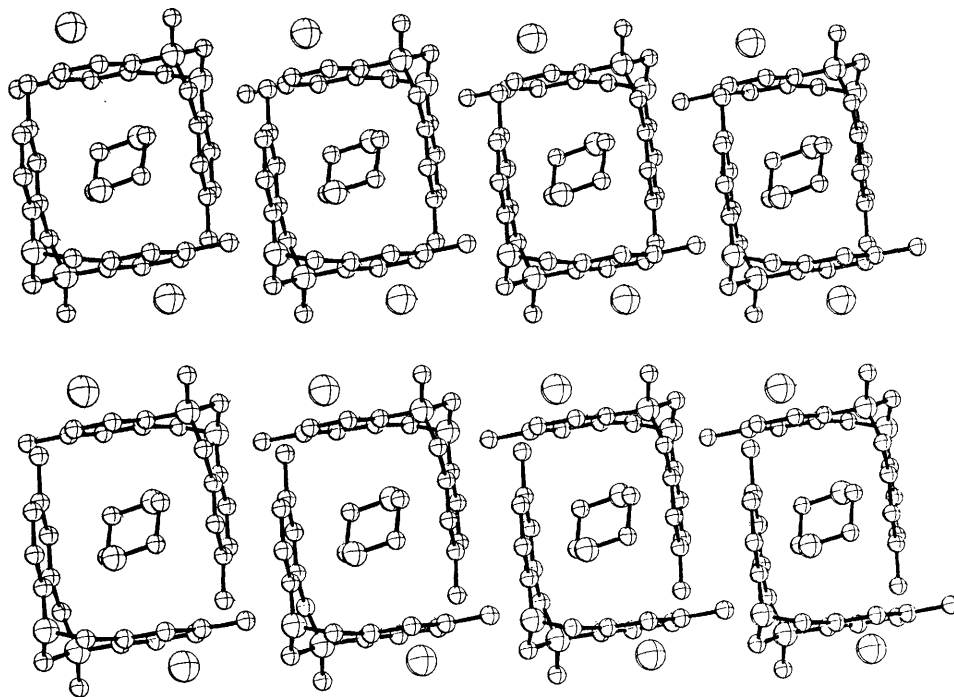
Compared to the free Tröger base (6), methylation as in (2b) alters the angle at the bridging methylene unit from 112 to 109°; differences in the other bonding dimensions are minor.

The present results may be understood as a further important example demonstrating the variability of onium compounds<sup>8</sup> as a new class of clathrate hosts. Since the Tröger base and analogous substituted derivatives belong to a particular type of chiral amines which therefore are separable into both optical antipodes,<sup>9</sup> enantiomeric guest inclusion,<sup>10</sup> especially for racemates of aromatic compounds, is a promising prospect.

¶ *Crystal data:* for (6), C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>, *M* = 284.34, light-yellow prisms from dioxane, monoclinic, space group *C*2/*c* (No. 15), *a* = 21.912(15), *b* = 8.290(6), *c* = 15.632(12) Å, β = 96.00(6)°, *U* = 2824.00 Å<sup>3</sup>, *Z* = 8, *F*(000) = 1199.79; graphite-monochromated Mo-*K*<sub>α</sub> radiation, μ(Mo-*K*<sub>α</sub>) = 0.82 cm<sup>-1</sup>, 2999 independent reflections with 0 < 2θ ≤ 40° recorded at 293 K, 988 unique observed reflections (*I* > 2.5σ), *R* = 0.036, *R*<sub>w</sub> = 0.039, {*w* = [σ<sup>2</sup>(*F*) + 0.0002 *F*<sup>2</sup>]<sup>-1</sup>} for 190 parameters.

For (2b)·0.5 dioxane, (C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>·I)·0.5C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, *M* = 436.31, light-yellow crystals from dioxane, triclinic, space group *P*1̄ (No. 2), *a* = 8.437(2), *b* = 9.485(2), *c* = 13.277(3) Å, α = 94.62(2)°, β = 99.08(2)°, γ = 105.15(2)°, *U* = 1004.41 Å<sup>3</sup>, *Z* = 2, *F*(000) = 439.94; graphite-monochromated Mo-*K*<sub>α</sub> radiation, μ(Mo-*K*<sub>α</sub>) = 15.83 cm<sup>-1</sup>, 2043 independent reflections with 0 < 2θ ≤ 40° recorded at 293 K, 1666 unique observed reflections (*I* > 2σ), empirical absorption correction by ψ-scans, *R* = 0.030, *R*<sub>w</sub> = 0.037 {*w* = [σ<sup>2</sup>(*F*) + 0.0005 *F*<sup>2</sup>]<sup>-1</sup>}, for 218 parameters.

All data were collected on a SYNTeX P21 four circle diffractometer using the ω-scan mode. Calculations were performed with SHELX-76.<sup>5</sup> The atomic co-ordinates for this work are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



**Figure 2.** Perspective view of the molecular packing in the  $(2b) \cdot 0.5$  dioxane clathrate. H atoms are omitted from this drawing.

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