

Synthesis and Inclusion Properties of the Host Compound 1,3-Dihydro-1,1,3,3-tetraphenylisobenzofuran. X-Ray Crystal Structures of the Free Host and of an Inclusion Compound with 1,4-Dioxane

EDWIN WEBER* and CLAUS WIMMER

*Institut für Organische Chemie der Technischen Universität Bergakademie Freiberg, Leipziger
Strasse 29, D-09596 Freiberg/Sachsen, Germany.*

INGEBORG CSÖREGH* and OLGA GALLARDO

*Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91
Stockholm, Sweden.*

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Abstract. A novel host molecule, **1**, suitable for crystalline lattice-type inclusion, has been synthesized, and its cocrystal formation ability has been investigated. Host **1** proved to be of potential use for organic solvent separation and retrieval, and a promising auxiliary for solidification of certain odorous substances. The crystal structures of the solvent-free host **1**, and its complex with 1,4-dioxane (1 : 1), have been determined by single crystal X-ray diffraction. The structure of **1** (guest-free) is triclinic, $P\bar{1}$, with $a = 9.452(2)$, $b = 10.359(3)$, $c = 13.116(3)$ Å, $\alpha = 101.80(2)$, $\beta = 106.53(1)$ and $\gamma = 104.32(1)^\circ$. The spacious, propeller-like molecules are held together by weak van der Waals' forces. The dioxane inclusion compound is monoclinic, $P2_1/a$, with $a = 15.050(1)$, $b = 8.641(1)$ and $c = 20.658(1)$ Å, and $\beta = 94.56(1)^\circ$, and contains two crystallographically independent guest molecules, both located around symmetry centres. The molecular packing seems to be governed by C—H \cdots O type bonds (C \cdots O = 3.31 and 3.48 Å) from the host to the dioxane oxygens.

Key words: Host synthesis, crystalline inclusion compounds, X-ray structure analysis, 1,4-dioxane guest.

Supplementary Data: Data relating to this article have been deposited with the British Library at Boston Spa, Wetherby, West Yorkshire, U.K., as Supplementary Publication No. SUP 82212 (15 pages).

1. Introduction

Crystalline inclusion compounds open up a wide area of application, especially the separation and retrieval of chemical species that differ in molecular shape, size, chemical nature or chirality [1]. This also includes new approaches to chemical sensor development [2]. Molecular imprisonment and environmental shielding is

* Authors for correspondence.

another advantage of crystalline inclusion formation that make toxic and hazardous substances safer [3]. Moreover, odorous substances and flavoring compounds may be solidified via inclusion, reducing their vapor pressure and volatility which makes controlled, retarded and suppressed release possible [3]. All this has stimulated great demand for compounds having the typical property of inclusion in the crystalline state (lattice hosts, clathrates) which are simple and easily obtainable [4].

In this context, we describe the synthesis of a new host compound **1**, report its crystal inclusion properties with reference to a variety of organic solvents and a collection of odorous terpene substances, and present the X-ray crystal structures of the free host **1** and of the inclusion compound of **1** with 1,4-dioxane guest (1 : 1).

2. Experimental

2.1. SYNTHESIS

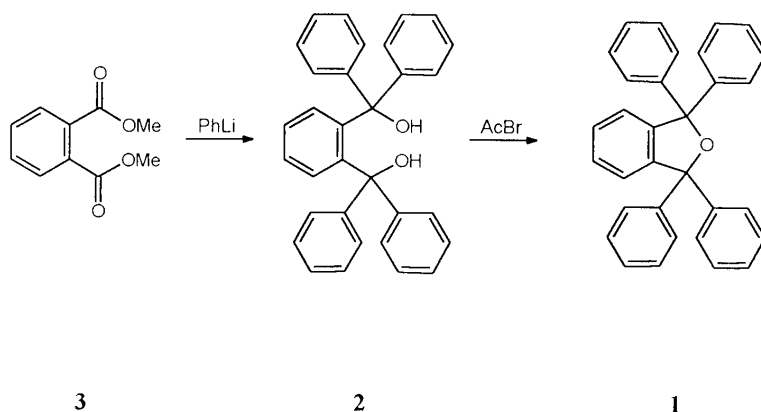
2.1.1. General

Melting points were obtained with a Kofler Apparatus (Reichert, Wien). ¹H-NMR spectra were taken with a WH-90 (90 MHz) (Bruker, Karlsruhe) in CDCl₃. Chemical shifts are reported in ppm downfield of tetramethylsilane as internal reference (s, singlet and m, multiplet). The mass spectra were recorded with an MS-50 spectrometer (A.E.I., Manchester).

2.1.2. Synthesis of host compound (**1**)

1,2-Bis(hydroxydiphenylmethyl)benzene (2). Phenyllithium reagent was prepared from 187.5 mL of a stirred solution of *n*-BuLi (1.6 M in *n*-hexane) to which was added dropwise a solution of 47.1 g (0.3 mol) bromobenzene in 300 mL dry diethyl ether at 0 °C and under argon. After stirring for 2 h at room temperature, the mixture was cooled to 0 °C, and 9.7 g (0.05 mol) dimethyl phthalate (**3**) was added dropwise. Stirring was continued for 4 h at room temperature. After quenching with an ice-cooled saturated solution of aqueous ammonium chloride, the aqueous phase was removed and extracted with three 100 mL portions of diethyl ether, and the combined organic layers were dried over sodium sulfate and filtered. Evaporation of the solvent and recrystallization from a 1 : 1 mixture of toluene/petroleum ether (40–60 °C) yielded 18.2 g (82%) of **2** as a colourless solid, m.p. 202 °C (lit. [5] 203.5 °C); ¹H-NMR δ 4.7 (s, 2H, OH), 6.6–7.5 (m, 24H, ArH); MS 424 (M⁺ – H₂O).

1,3-Dihydro-1,1,3,3-tetraphenylisobenzofuran (1). A mixture of 4 g (9 mmol) of compound **2** and 13.4 mL (180 mmol) of acetyl bromide were heated under reflux for 35 min. After cooling, the mixture was hydrolyzed by slow addition of 25 mL of water. The aqueous phase was extracted with chloroform, and the combined organic layers were dried over sodium sulfate, filtered and evaporated to dryness. Recrystallization from chloroform/petroleum ether (60–90 °C) yielded 1.52 g (40%) of



Scheme 1.

Table I. Crystalline solvent inclusion compounds of **1**.^{a,b}

Dimethyl sulfoxide (1 : 1), cyclohexanone (1 : 1), *n*-propylamine (2 : 1), piperidine (3 : 1), morpholine (1 : 1), tetrahydrofuran (2 : 1), 1,4-dioxane (1 : 1), pyridine (1 : 1), benzene (1 : 1), toluene (1 : 1), xylene (2 : 1), cyclohexene (2 : 1), cyclohexane (2 : 1).

^a See the Experimental section for method of preparation, drying standard, and characterization; stoichiometric ratios (host : guest) are given in parentheses.

^b The following solvents yielded no inclusion compound under the experimental conditions: methanol, ethanol, isopropanol, *t*-butanol, cyclohexanol, acetone, acetonitrile, nitromethane, dimethylformamide, cyclohexylamine, di-*n*-propylamine, mesitylene, methylcyclohexane.

1 as a colourless solid, m.p. 174 °C; ¹H-NMR δ 7.0–7.2 (m, 2OH, Ph–H), 7.4 (s, 4H, ArH); MS 424 (M⁺).

2.1.3. Crystalline inclusion compounds

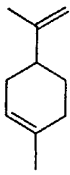
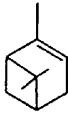
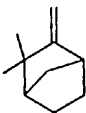
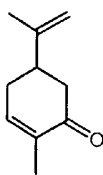
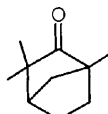
The host compound was dissolved with heating in a minimum amount of the appropriate guest solvent or terpene. After storage for 12 h at room temperature, the crystals which formed were collected, washed with diethyl ether, and dried (1 h, 15 Torr, room temperature). Host : guest stoichiometric ratios were determined by ¹H-NMR integration. Data for each compound are given in Tables I and II.

2.2. CRYSTALLOGRAPHY

2.2.1. Sample preparation

Single crystals of compound **1** and **1** · 1,4-dioxane (1 : 1) were obtained by dissolution of **1** in chloroform/petroleum ether (60–90 °C) or 1,4-dioxane, and saturating the solution by slow evaporation at room temperature.

Table II. Crystalline inclusion compounds of **1** with terpene odorous substances.^a

				
Limonene	β -Pinene	Camphene	Carvone	Fenchone
(2:1)	(2:1)	(2:1)	(1:1)	(1:1)

^a See the Experimental section for method of preparation, drying standard, and characterization; stoichiometric ratios (host : guest) are given in parentheses.

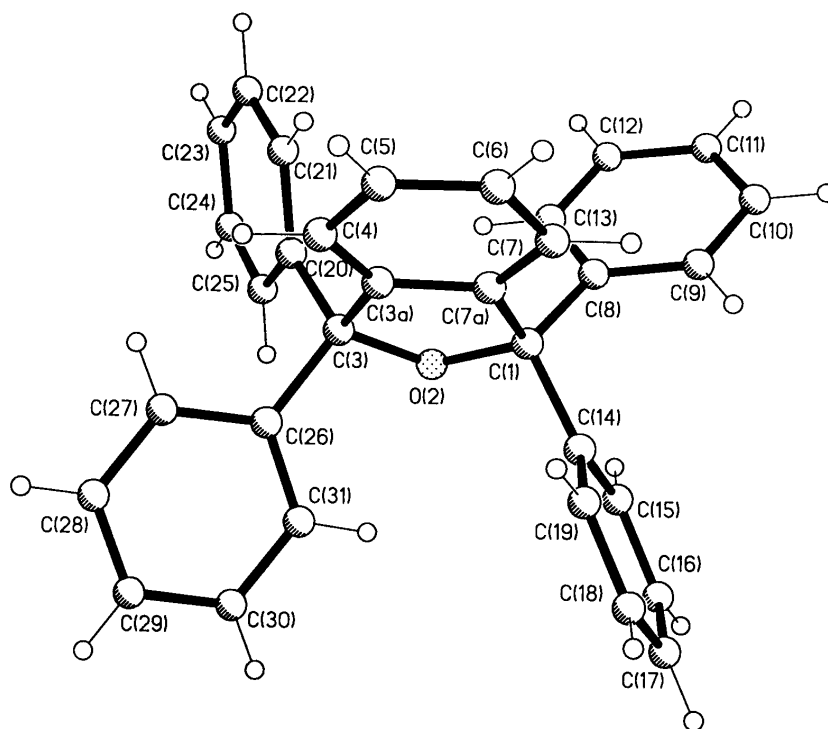


Figure 1. Perspective view of host molecule **1** in the solvent-free crystal, with the crystallographic numbering of the non-hydrogen atoms.

2.2.2. X-Ray data collection and processing

The reflection intensities were measured by the ω - 2θ scan technique, using a STOE/AED2 diffractometer equipped with a graphite monochromator. Data reduc-

Table III. Crystal data and selected experimental details. The esd's, where given, are in parentheses.

Compound	1 (guest-free)	1 · 1,4-dioxane (1 : 1)
Formula unit	C ₃₂ H ₂₄ O	C ₃₂ H ₂₄ O · C ₄ H ₈ O ₂
Formula weight	424.54	512.65
Symmetry	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>a</i> (No. 14)
Unit cell dimensions		
<i>a</i> , Å	9.452(2)	15.050(1)
<i>b</i> , Å	10.359(3)	8.641(1)
<i>c</i> , Å	13.116(3)	20.658(1)
α, deg	101.80(2)	90
β, deg	106.53(1)	94.56(1)
γ, deg	104.32(1)	90
<i>V</i> _c , Å ³	1139.5(5)	2678.0(4)
Refinement of the cell dimensions		
No. of θ values used	42	37
2θ -range, deg	19–43	11–34
<i>Z</i>	2	4
<i>F</i> (000)	448	1088
<i>D</i> _c , mg m ⁻³	1.2373(6)	1.2715(2)
μ , cm ⁻¹	5.61	0.794
Radiation/ λ , Å	CuK α /1.54183	MoK α /0.71069
Temperature, K	291 ± 1	173 ± 1
Approximate crystal size, mm	0.06 × 0.09 × 0.22	0.30 × 0.27 × 0.19
No. of collected reflections	3326	8401
θ limit, deg	1–60	1–30
Range of <i>h</i> , <i>k</i> and <i>l</i>	–10 → 10, –11 → 11, 0 → 14	–21 → 21, 0 → 12, 0 → 29
No. of unique reflections	3326	6180
<i>R</i> _{int}	–	0.0285
No. of standard reflections	5	4
Time interval between the standards, min	90	90
Intensity instability	<2%	<4.2%
Refinement method: full-matrix least-squares based on	<i>F</i> ² ^a	<i>F</i> ^b
No. of refined parameters	323	384
(Δ/σ) _{max}	0.044	0.033
Final <i>R</i> indices		
<i>R</i> (= $\Sigma \Delta F /\Sigma F_0 $)	0.044	0.037
no. of reflections used	1261	2276
with the limits	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 3σ(<i>I</i>)
<i>wR</i> ^a , based on <i>F</i> ²	0.112	
no. of <i>F</i> ² values used	3300	
Goodness-of-fit on <i>F</i> ²	0.886	
<i>wR</i> ^b , based on <i>F</i>		0.045
no. of <i>F</i> values used		2276
Final $\Delta\rho_{\max}/\Delta\rho_{\min}$, e, Å ⁻³	0.16/–0.19	0.21/–0.23

^a According to the SHELXL-93 program [7]. The weights of the observations were calculated as $w = 1/[\sigma^2(F_0^2) + 0.0423P^2]$ where $P = (F_0^2 + 2F_c^2)/3$.

^b According to the SHELX-76 program [8]. The weights of the structure factors were assumed as $w = 0.744/[\sigma^2(F) + 0.0010 \cdot F^2]$.

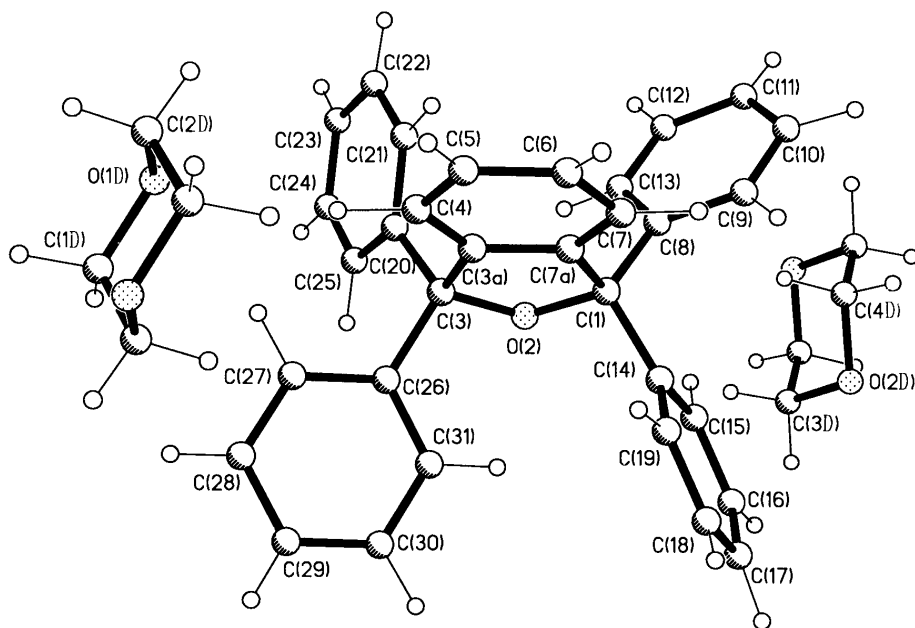


Figure 2. Perspective view of host **1** with the two crystallography independent dioxane guest molecules, as observed in the crystalline **1** · 1,4-dioxane (1 : 1) compound. The unique non-hydrogen atoms (cf. Table III) are labelled as in the text.

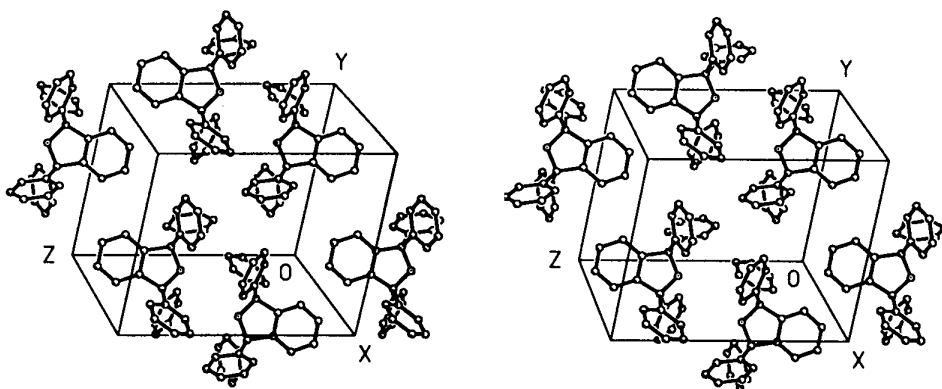


Figure 3. Stereoscopic packing illustration of the crystal of **1** (guest free). The H atoms are omitted for clarity.

tion involved corrections for background, intensity deterioration, and Lorentz and polarization effects (cf. Table III).

Table IV. Fractional atomic coordinates of the non-hydrogen atoms of compounds **1** and **1** · 1,4-dioxane (1 : 1), with esd's in parentheses.

Atom	x/a	y/b	z/c
Compound 1 (guest free)			
C(1)	0.3416(4)	0.8974(3)	0.2397(3)
O(2)	0.3516(3)	0.7989(2)	0.3044(2)
C(3)	0.3729(4)	0.6730(3)	0.2471(3)
C(3a)	0.3733(4)	0.6960(4)	0.1364(3)
C(4)	0.3847(5)	0.6102(4)	0.0453(3)
C(5)	0.3909(5)	0.6585(4)	-0.0448(3)
C(6)	0.3829(5)	0.7885(5)	-0.0443(3)
C(7)	0.3674(4)	0.8728(4)	0.0445(3)
C(7a)	0.3608(4)	0.8256(4)	0.1348(3)
C(8)	0.4755(4)	1.0338(4)	0.3037(3)
C(9)	0.4705(5)	1.1558(4)	0.2783(3)
C(10)	0.5942(5)	1.2786(4)	0.3300(3)
C(11)	0.7249(5)	1.2815(4)	0.4110(4)
C(12)	0.7330(5)	1.1617(4)	0.4386(4)
C(13)	0.6068(5)	1.0381(4)	0.3852(3)
C(14)	0.1811(4)	0.9149(4)	0.2223(3)
C(15)	0.1525(5)	0.9847(4)	0.3123(4)
C(16)	0.0069(5)	0.9955(4)	0.3014(4)
C(17)	-0.1117(6)	0.9372(5)	0.2015(5)
C(18)	-0.0870(5)	0.8683(4)	0.1116(4)
C(19)	0.0602(5)	0.8568(4)	0.1226(4)
C(20)	0.5279(4)	0.6666(3)	0.3196(3)
C(21)	0.6581(5)	0.6830(4)	0.2911(4)
C(22)	0.7975(5)	0.6846(4)	0.3638(4)
C(23)	0.8081(5)	0.6700(4)	0.4661(4)
C(24)	0.6791(5)	0.6550(4)	0.4969(4)
C(25)	0.5383(5)	0.6518(4)	0.4249(3)
C(26)	0.2388(4)	0.5475(4)	0.2348(3)
C(27)	0.2428(5)	0.4127(4)	0.1997(3)
C(28)	0.1237(5)	0.2977(4)	0.1913(3)
C(29)	0.0008(5)	0.3148(4)	0.2182(4)
C(30)	-0.0066(5)	0.4457(4)	0.2522(4)
C(31)	0.1103(5)	0.5604(4)	0.2592(3)

2.2.3. Structure analysis and refinement

The non-hydrogen atoms, located by application of direct methods (SHELXS) [6], were treated anisotropically, whereas isotropic vibration parameters were refined for the hydrogens in both compounds. The H atoms of the guest-free host **1** were

Table IV. Continued.

Atom	x/a	y/b	z/c
Compound 1 · 1,4-dioxane (1 : 1)			
C(1)	0.2698(2)	0.7022(4)	0.1926(1)
C(2)	0.2146(1)	0.6889(2)	0.2475(1)
C(3)	0.2517(2)	0.7707(3)	0.3048(1)
C(3a)	0.3379(2)	0.8377(3)	0.2838(1)
C(4)	0.4012(2)	0.9271(4)	0.3192(1)
C(5)	0.4765(2)	0.9718(4)	0.2897(2)
C(6)	0.4886(2)	0.9287(4)	0.2263(1)
C(7)	0.4250(2)	0.8409(4)	0.1904(1)
C(7a)	0.3488(2)	0.7969(3)	0.2199(1)
C(8)	0.2163(2)	0.7883(4)	0.1374(1)
C(9)	0.2518(2)	0.8057(4)	0.0772(1)
C(10)	0.2071(2)	0.8909(4)	0.0281(2)
C(11)	0.1255(2)	0.9601(4)	0.0376(2)
C(12)	0.0888(2)	0.9390(4)	0.0958(2)
C(13)	0.1338(2)	0.8566(3)	0.1460(1)
C(14)	0.2913(2)	0.5365(3)	0.1743(1)
C(15)	0.3742(2)	0.4692(4)	0.1901(2)
C(16)	0.3874(3)	0.3116(4)	0.1810(2)
C(17)	0.3174(3)	0.2189(4)	0.1556(2)
C(18)	0.2353(3)	0.2845(4)	0.1388(2)
C(19)	0.2224(2)	0.4418(4)	0.1476(1)
C(20)	0.1823(2)	0.8925(4)	0.3199(1)
C(21)	0.1872(2)	1.0427(4)	0.2966(2)
C(22)	0.1170(2)	1.1458(4)	0.3022(2)
C(23)	0.0413(2)	1.0993(4)	0.3305(2)
C(24)	0.0358(2)	0.9507(4)	0.3545(2)
C(25)	0.1063(2)	0.8481(4)	0.3497(2)
C(26)	0.2716(2)	0.6524(4)	0.3598(1)
C(27)	0.2890(2)	0.7028(4)	0.4237(1)
C(28)	0.3144(2)	0.5985(4)	0.4728(2)
C(29)	0.3237(2)	0.4426(4)	0.4588(2)
C(30)	0.3053(2)	0.3912(4)	0.3960(2)
C(31)	0.2795(2)	0.4951(4)	0.3464(2)
O(1D)	0.4191(2)	1.0773(3)	0.4817(1)
C(1D)	0.4253(2)	0.9647(4)	0.5320(2)
C(2D)	0.5036(2)	1.1510(5)	0.4794(2)
O(2D)	0.0736(1)	0.3976(3)	0.0029(1)
C(3D)	-0.0006(2)	0.3716(4)	0.0404(2)
C(4D)	0.0838(2)	0.5603(4)	-0.0072(2)

Table V. Selected conformational features^a of host molecule **1**, as observed in its solvent free crystal and in the inclusion compound with the dioxane guest (1 : 1). ESD's are given in parentheses.

Compound	1 (guest free)	1 · 1,4-dioxane (1 : 1)
Planarity of the ring fragments: the ring atoms are co-planar to within, Å		
Dihydrofuran ring (1)	0.035(4)	0.022(3)
C(3a) ··· C(7a) benzene ring (2)	0.028(5)	0.018(3)
1,3-Dihydroisobenzofuran moiety (3)	0.083(5)	0.052(3)
C(8) ··· C(13) phenyl ring (4)	0.014(5)	0.032(3)
C(14) ··· C(19) phenyl ring (5)	0.005(5)	0.017(3)
C(20) ··· C(25) phenyl ring (6)	0.012(4)	0.017(3)
C(26) ··· C(31) phenyl ring (7)	0.016(5)	0.017(3)
Dihedral angles formed by the least-squares ring planes, deg		
Rings (1) and (2)	2.7(1)	1.7(1)
Rings (3) and (4)	71.3(1)	67.3(1)
Rings (3) and (5)	72.4(1)	73.1(1)
Rings (3) and (6)	69.3(1)	79.3(1)
Rings (3) and (7)	59.6(1)	74.5(1)
Rings (4) and (5)	76.8(1)	89.4(1)
Rings (6) and (7)	83.0(1)	76.7(1)
Rings (4) and (6)	69.4(1)	45.1(1)
Rings (5) and (7)	65.3(2)	58.9(1)
Rings (4) and (7)	59.8(1)	60.6(1)
Rings (5) and (6)	37.8(1)	49.9(1)

^a Calculated with the program PARST [10].

assumed to be in idealized positions, calculated using geometric evidence, taking into account the effects of both the chemical environment and the temperature (SHELXL-93) [7]. The hydrogen positions in the inclusion compound **1** · 1,4-dioxane (1 : 1), on the other hand, were derived from the difference electron density ($\Delta\rho$) map (SHELX-76) [8], and were held riding on their parent carbon atoms during the subsequent calculations. Details of the structure refinements together with the final R values are shown in Table III. It is worth mentioning that it proved to be difficult to find a single crystal of the solvent-free host **1** that was of acceptable quality for X-ray diffraction analysis. Less than 38% of the collected unique intensity data had $I > 2\sigma(I)$, and in the last refinement of that structure, 26 reflections were omitted due to potential systematic errors. Moreover, the F_c values were corrected by the function $\mathbf{k}[1 + 0.001 \cdot \mathbf{x} \cdot F_c^2 \cdot \lambda^3/\sin(2\theta)]^{-1/4}$, where \mathbf{k} is the overall scale factor and \mathbf{x} is an extinction parameter [7], which in case of **1** refined to 0.0055(5).

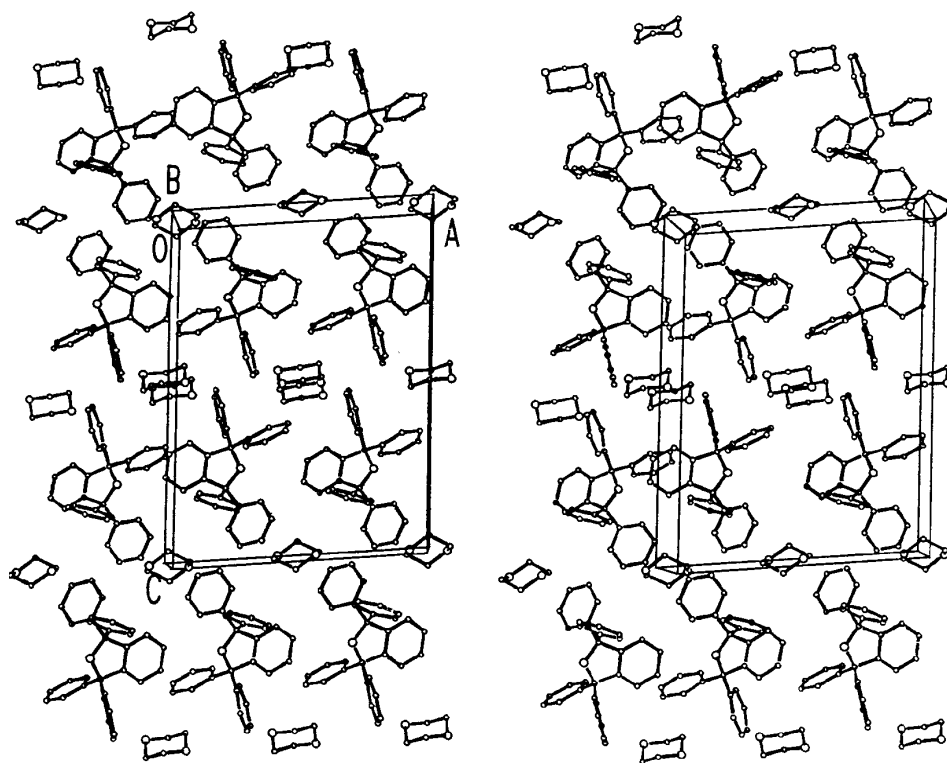


Figure 4. Stereoscopic packing illustration of the **1** · 1,4-dioxane (1 : 1) crystal. The H atoms are omitted for clarity.

3. Results and Discussion

3.1. INCLUSION PROPERTIES

Although molecule **1** has a structure typical of a crystalline lattice host, i.e. a rigid and bulky framework [9], its chemical nature as a rather apolar substance makes inclusion of strong H-bond acceptor and donor solvents rather unlikely. This is exactly what was found (Table I), since neither alcohols nor ordinary amines (except di-*n*-propylamine) are included. On the other hand, aprotic and largely apolar organic compounds are readily included, ranging from DMSO to cyclohexane (Table I). Although morpholine and piperidine may also be considered as H-bond donors, the efficiency of these compounds as guests is probably due to the shape and size of the molecules, i.e. a six-membered ring, rather than to their functionality. Actually, it appears that molecules having a six-membered ring constitution are guests that are preferentially accommodated in the lattice of **1**, regardless of their chemical nature. Ten of the thirteen different inclusion species listed in Table I thus involve a guest molecule that features a six-membered ring. Moreover, the results in Table I demonstrate that substitution on the ring is tolerated only to a certain

Table VI. Geometric parameters of possible intermolecular interactions in crystals of **1** (solvent free) and **1** · 1,4-dioxane (1 : 1). The esd's, where given,^a are in parentheses.

A. Intermolecular contact distances (Å) less than 3.6 Å between the non-hydrogen atoms.

Atoms	Symmetry	Distance			
1 (solvent free)					
C(6)···C(29)	$-x, -y + 1, -z$	3.446(6)			
C(17)···C(21)	$x - 1, y, z$	3.597(7)			
1 · 1,4-dioxane(1 : 1)					
O(2)···C(6)	$x - 0.5, -y + 1.5, z$	3.544(4)			
C(5)···C(25)	$x + 0.5, -y + 1.5, z$	3.550(5)			
C(4)···O(1D)	x, y, z	3.589(4)			
C(10)···O(2D)	$-x + 0.5, y + 0.5, -z$	3.411(4)			
C(10)···C(4D)	x, y, z	3.453(5)			
C(10)···C(4D)	$-x + 0.5, y + 0.5, -z$	3.528(5)			
C(28)···C(2D)	$-x + 1, -y + 2, -z + 1$	3.569(5)			
C(30)···O(1D)	$x, y - 1, z$	3.597(4)			
B. Distances (Å) and angles (deg) in possible C—H···O bonds.					
Atoms involved	Symmetry	Distances			Angle
		C···O	C—H	H···O	<C—H···O
1 · 1,4-dioxane (1 : 1)					
C(9)—H(9)···O(2D)	$-x + 0.5, y + 0.5, -z$	3.311(4)	0.92	2.73	122
C(29)—H(29)···O(1D)	$x, y - 1, z$	3.485(4)	0.97	2.80	129

^a The H atom positions were not refined (cf. text).

limit (cf. xylene vs. mesitylene or cyclohexane vs. methylcyclohexane). Hence, crystalline inclusion formation by **1** with the usual organic solvent molecules is subject to effective control by polarity and shape parameters. The stoichiometric ratios (host : guest) are certainly connected with this point, but there is no clear evidence to be obtained from the results.

In a sense, the inclusion compounds **1** forms with odorous terpene substances (Table II) is at variance with the previous statements, in that these guests are molecules of rather high degree of substitution or bridging in the six-membered ring frame. Nevertheless, these compounds show a clear relation between the chemical nature of the guest molecule and the host : guest stoichiometric ratio of the complexes. All the inclusion compounds of pure hydrocarbon terpenes (limone, β -pinene, camphene) exhibit a 2 : 1 host : guest stoichiometric ratio, whereas the ketones carvone and fenchone yield 1 : 1 host : guest inclusion compounds with **1**. From this point of view, the previously mentioned solvent inclusion compounds of **1** (Table I) are then in conformity (cf. cyclohexane or cyclohexene vs. cyclohexanone).

Referring to the introduction, the present crystal inclusion compounds illustrate that host compound **1** is both of potential use for organic solvent separation

and retrieval, and as a promising auxiliary for solidification of certain odorous substances, which will allow retarded release of the lemon, spruce-needle, caraway/dill or fennel aroma typical of the mentioned terpenes.

3.2. STRUCTURAL STUDIES

3.2.1. *Molecular structures*

As can be seen in Figures 1 and 2, the host molecule **1** exhibits similar conformations in the solvent-free crystal and in its dioxane (1 : 1) inclusion compound. The bicyclic dihydroisobenzofuran moiety is approximately flat and rather stiff, and the single-bonded phenyl substituents seem to have a limited possibility ($\sim \pm 10^\circ$) to rotate around their $C_{\text{furan}}-C_{\text{phenyl}}$ linkage due to proximity and steric hindrance (cf. Table V). Hence, molecule **1** has a spacious, propeller-like semi-rigid shape, suitable for lattice type inclusion formation.

There are two crystallographically non-equivalent dioxane guests in the **1** · 1,4-dioxane (1 : 1) crystal, both located around inversion centres. Thus, the asymmetric crystallographic unit of this structure consists of one host and two halves of two guest molecules (Figure 2). The dioxane rings show the usual chair conformation. The ring puckering parameters [11] are $q_2 = 0(0.004)$ and $0(0.004)$ Å, $q_3 = 0.575(3)$ and $-0.569(3)$ Å, $\phi_2 = -58.6$ and -103.4° , $Q_T = 0.575(3)$ and $0.569(3)$ Å, and $\theta_2 = 0(0.4)$ and $180(0.4)^\circ$, calculated [10] for the molecules containing O(D1) and O(D2), respectively.

Bond distances and angles generally conform to expected values in both structures (see Table V).

3.2.2. *Packing relations*

Molecule **1** has low polarity and very limited proton donor ability, and its shape is inconvenient for close packing on its own. It proved to be difficult to grow single crystals of the solvent-free host with acceptable crystal quality. Investigation of the intermolecular contacts indicates that molecules of **1** (Figure 3) are held together by weak van der Waals' forces, which rarely give rise to contact distances shorter than 3.6 Å between the non-hydrogen atoms (Table VI). This observation is in agreement with the relatively low crystal density ($D_c = 1.237 \text{ g cm}^{-3}$) calculated for this compound.

As a consequence, molecule **1** readily forms cocrystals with space-filling guests of the right size and shape. 1,4-Dioxane seems to be such a suitable guest. In the crystalline lattice-type inclusion compound several intermolecular distances shorter than 3.6 Å were observed between the non-hydrogen atoms (Table V), in accordance with the increased crystal density ($D_c = 1.272 \text{ g cm}^{-3}$), as compared with that of the solvent-free host. The host molecules in the inclusion compound are arranged so as to form layers parallel to the crystallographic *ab* plane, stacked one upon the other in the crystallographic *c* direction. The guests are located in

the voids between the host layers. Most of the close approaches (Table V) were observed between host and guest molecules. Although host **1** is a 'non-protonic' compound, the dioxane guests are oriented in the crystal so that each dioxane oxygen can take advantage of a possible C—H ··· O bond from a neighbouring host, in agreement with the twofold proton acceptorship of the dioxane molecule [12]. Hence, the crystal of the dioxane inclusion compound seems to be stabilized by an electrostatically favourable molecular packing besides the ordinary van der Waals' forces.

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