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HOST-GUEST COMPOUNDS. X-RAY STRUCTURE, DIFFERENTIAL SCANNING CALORIMETRY, AND THERMOGRAVIMETRY OF METHANOL, ETHANOL, ISOPROPANOL, TERT-BUTANOL AND DIOXANE INCLUSION COMPOUNDS IN 7-BENZOYL-6-PHENYL-6,7-DIHYDRO-1-METHYL-3-METHYLTHIO-5H-1,2,4-TRIAZOLO[3,4-b][1,3,4]THIADIAZINIUM BROMIDE.

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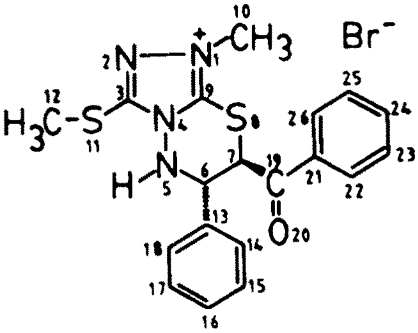
Abstract.- The crystal structures of 1a, 1.MeOH, 1b, 1.EtOH, 1c, 1.iPrOH and 1d, 1.2-tBuOH, 1 being 7-benzoyl-6-phenyl-6,7-dihydro-1-methyl-3-methylthio-5H-1,2,4-triazolo[3,4-b][1,3,4]thiadiazinium bromide, have been studied by X-ray diffraction. They crystallize in the space groups $P2_{1/c}$, $P2_{1/c}$, C2/c and $P\bar{1}$, respectively, the cell constants being: 11.8790(6), 15.1735(14), 12.6975(9) Å, 90, 98.036(4), 90° for 1a; 11.9894(2), 15.2223(4), 13.0151(3) Å, 90, 96.631(2), 90° for 1b; 20.1583(6), 12.2180(3), 20.8012(6) Å, 90, 105.017(2), 90° for 1c; 12.2747(4), 14.0487(5), 10.1274(3) Å, 94.861(2), 113.728(3), 90.087(3)° for 1d. The four cystals build up with units of "1.alcohol", quite similar in the four compounds. The host-guest packing schemes are also analyzed. The geometries, including the conformation, of the guest alcohols are compared with experimental and theoretical data from the literature. Some discrepances are observed, but the X-ray analysis of structures containing inclusion compounds, which are liquids at room temperature, seems to be a useful approach, within some stated limits, for studying such compounds.

Introduction.- Experimental molecular geometries provide the most secure basis for structural chemistry. Of all the techniques which have been used to obtain this information (microwave spectroscopy, electron diffraction, n.m.r. in nematic phases...), X-ray crystallography alone has contributed with more structures than all the other methods together. The only condition required for an X-ray analysis is the obtention of suitable single crystals. Normally, this has limited the structures to compounds melting above room temperature. Comparatively few structures of compounds melting below 25°C have been determined (by low-temperature X-ray crystallography) as can be noticed from a search in the CDF[1] (1986 version).

This situation encouraged us to study the possibility of determining the structure of molecules, liquid at room temperature, included in crystalline cavities. There are many compounds which crystallize with one or more solvent molecules. Usually, these molecules of solvent (water, chloroform, methylene chloride...) are considered more as a nuisance than as a source of useful information. We propose to reverse this situation and to draw the attention to the guest. The idea is to change the nature of the guest, keeping the host constant. Usually, this change produces modifications in the arrangement of the so called host molecule, although the "host-guest" terminology is not strictly describing the co-crystallization processes, where both entities are able to rearrange more freely their relative positions, without the cavity limitations of true inclusions compounds or cavities[2]. For lattice-type inclusions compounds (no host cavity) the influence of the solvent crystallization molecules on the whole structure can vary from dramatic to almost unnoticeable. So it is worth studying on the one hand the conformation of guest compounds of low molecular weight, and on the other hand the variation of the host lattice and the conformation of the host molecule.



1

a, CH_3OH
b, C_2H_5OH
c, i-C_3H_7OH
d, t-C_4H_9OH

Scheme 1

In order to evaluate the possibilities of these ideas, we have selected as host 7-benzoyl-6-phenyl-6,7-dihydro-1-methyl-3-methylthio-5H-1,2,4-triazolo [3,4-b][1,3,4]thiadiazinium bromide 1, a molecule which we have already established, that crystallized with 0.5 dioxane molecules[3]. As guests, the classical sequence, methanol, ethanol, i-propanol and t-butanol, was selected since the geometries of these compounds are well-known both from an experimental and a theoretical point of view.

It must be emphasized that there are very few examples of ionic hosts[2], although the stability of the ionic host lattice is certainly of significance for the clathrate properties. In Weber nomenclature[2] lattice type-inclusion alcohols in an ionic guest lattice belong to the "coordinatoclathrate" class.

Experimental.- Compound 1, carefully dried under vacuum at 120°C to eliminate crystallization dioxane[3], was dissolved in the corresponding alcohol. By slow evaporation, crystals of 1a, 1b, 1c and 1d were obtained.

Differential scanning calorimetry (DSC) and thermogravimetry (TG) studies were carried out under nitrogen on a Mettler DSC-20 calorimeter and a Mettler TG-50 thermobalance. The results are gathered in Table 5.

Proton n.m.r. spectra were recorded at 300 MHz on a Varian XL-300 supraconducting spectrometer.

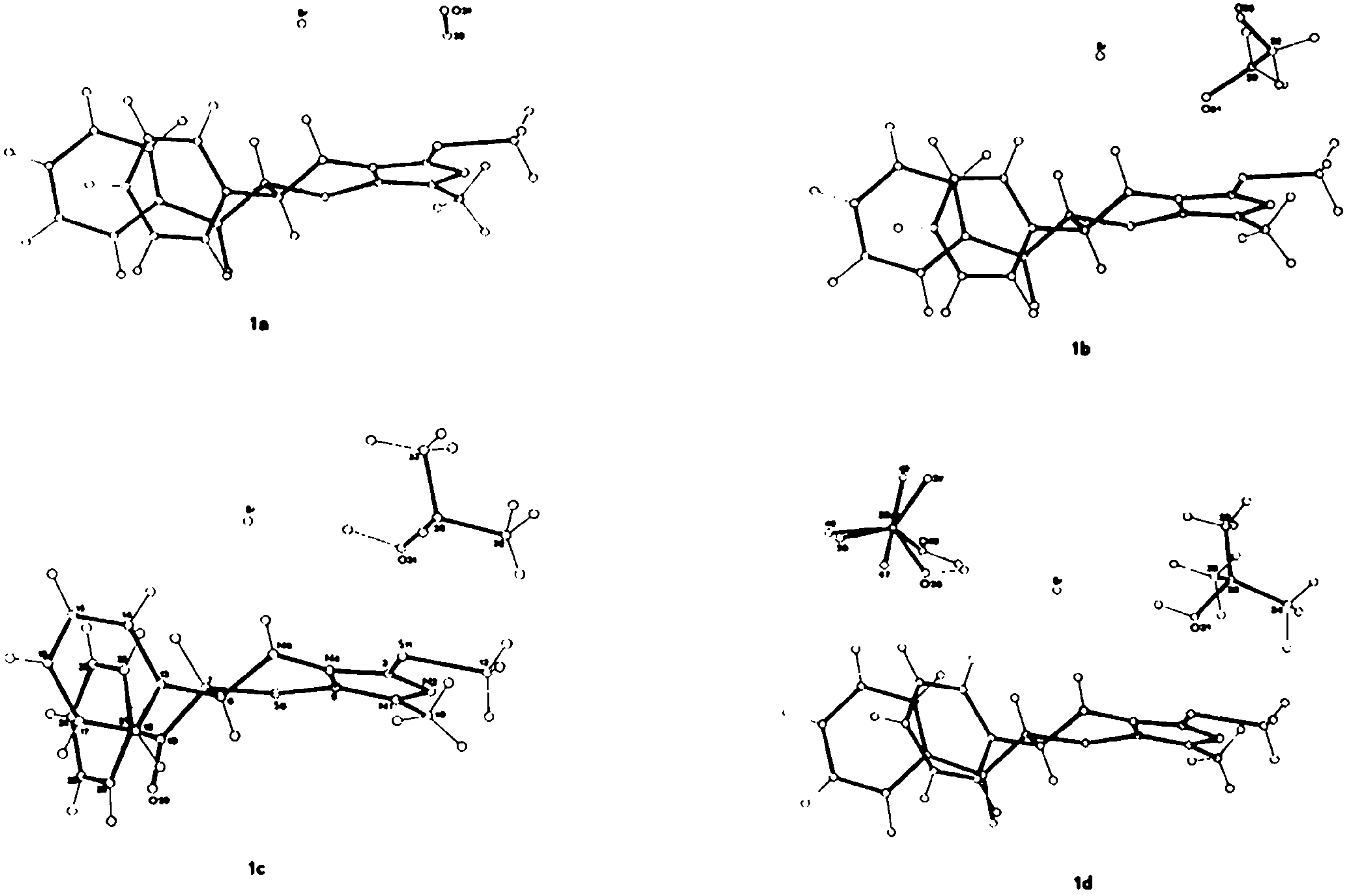
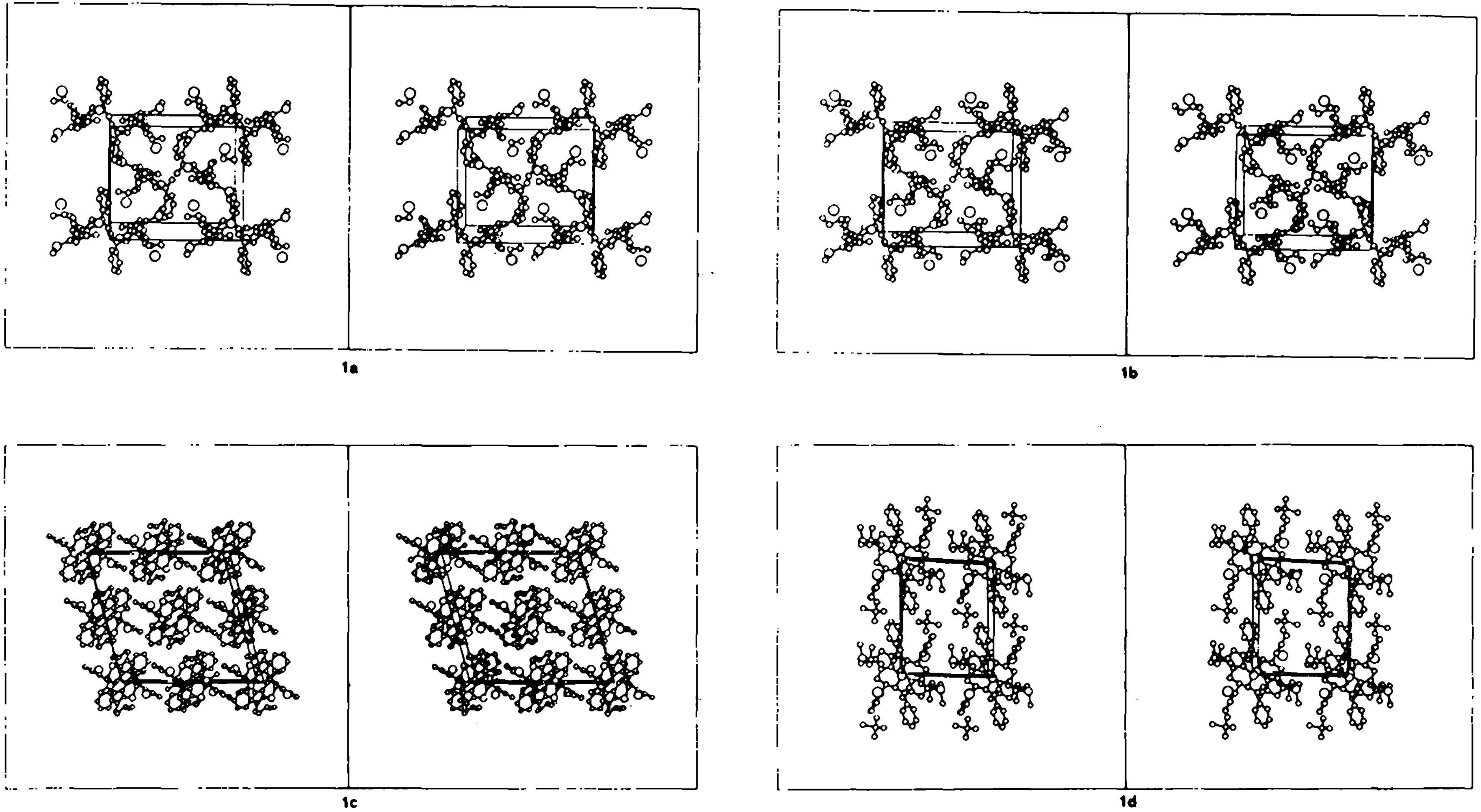


Fig. 1. Crystal structures of compounds 1a, 1b, 1c (showing the common atomic numbering) and 1d[27].



1a

1b

1c

1d

Fig. 2. Stereoscopic view of the unit cell of compounds 1a, 1b, 1c and 1d. Hydrogen atoms have been omitted for the sake of clarity[28]

Crystal Data at Room Temperature. 1a: $C_{19}H_{19}N_4OS_2Br.(CH_4O)$, Monoclinic, $P2_{1/c}$, Z=4, D_x=1.449 $Mg.m^{-3}$, a=11.8790(6), b=15.1735(14), c=12.6975(9) Å, β=98.036(4)°, (from least-squares fit of the 2θ values of 84 reflections with θ up to 45° with CuK_α radiation), Mr=494.44, V=2266.2(3) $Å^3$, F(000)=1012, μ=4.374 mm^{-1} (Mx. and min. transmission factors 1.209-0.803)[4]. A colourless transparent square prism of 0.27x0.08x0.07 mm was used in the analysis.

1b: $C_{19}H_{19}N_4OS_2Br.(C_2H_6O)$, Monoclinic, $P2_{1/c}$, Z=4, D_x=1.434 $Mg.m^{-3}$, a=11.9894(2), b=15.2223(4), c=13.0151(3) Å, β=96.631(2)° (94 reflections), Mr=509.48, V=2359.5(1) $Å^3$, F(000)=1048, μ=4.216 mm^{-1} (Mx and min. 1.202-0.743). Colourless transparent square prism of 0.40x0.27x0.10 mm dimensions.

1c: $C_{19}H_{19}N_4OS_2Br.(C_3H_8O)$, Monoclinic, C2/c, Z=8, D_x=1.405 $Mg.m^{-3}$, a=20.1583(6), b=12.2180(3), c=20.8012(6) Å, β=105.017(2)° (82 reflections), Mr=523.51, V=4948.3(2) $Å^3$, F(000)=2160, μ=4.034 mm^{-1} (Mx. and min. 1.143-0.703). Colourless transparent hexagonal plate of dimensions (0.30x0.17x0.30)x0.07 mm.

1d: $C_{19}H_{19}N_4OS_2Br.2(C_4H_{10}O)$, Triclinic, P_1, Z=2, D_x=1.276 $Mg.m^{-3}$, a=12.2747(4), b=14.0487(5), c=10.1274(3) Å, α=94.861(2)°, β=113.728(3)°, γ=90.087(3)° (92 2θ values for the fit), Mr=611.65, V=1591.8(1) $Å^3$, F(000)=640, μ=3.226 mm^{-1} (Mx. and min. 1.215-0.749). Colourless transparent square prism of dimensions 0.40x0.23x0.10 mm.

Data Collection and Processing. Philips PW1100 diffractometer, ω/2θ scans, width 1.5°, graphite monochromated Cu-K_α radiation, θ up to 65°, about 1 min/reflx. Stability checked every 90 min. using two standard reflections. Lorentz and polarization correction applied. 3σ(I) criterion for the unobserved reflections. These were the conditions for the four cases. The number of total independent (and observed) reflections were 3838(2470), 3990(3456), 4205(3082) and 5405(4684) respectively for the four compounds. The (h, k, l) ranges were [±14, 0-18, 0-15], [±14, 0-18, 0-15], [±19, 0-14, 0-23] and [±14, ±17, 0-11].

Analysis and Refinement of the Structure. Patterson and Direct Difference Methods[5] and weighted full matrix least-squares refinement[5] were used together with empirical absorption correction[4]. Anitropic model for the non-hydrogen atoms and isotropic one for the hydrogen atoms were used. Hydrogen atoms were located from difference synthesis, some of them could not be located (see below). Weights are chosen with empirical functions on F_0 and sin θ/λ as to give no trend in $<w\Delta^2F>$ vs. $<F_0>$ and <sinθ/λ>.

1a: The methanol compound is pseudoisomorphous of 1b, the hydrogen atoms of the methanol group could not been located and were not included in the calculations, 388 parameters, final R and R_w factors were 0.069, 0.071, final residual density 0.90 $eÅ^{-3}$, maximum thermal value U_{22}[C(30)] 0.32(4) $Å^2$, and last mean shift/error was 0.27.

1b: The ethanol molecule presents twofold disorder but with coincident carbon positions, so two hydrogen atoms (those along the C-O bond, see Fig. 1.b) could not be located, and neither the hydroxyl hydrogens; none of them were used for the structural factors calculation; the populations were estimated as 0.52(2) and 0.48(2). 374 variables, final R's 0.047, 0.054, final residual density, 0.35 $eÅ^{-3}$, maximum thermal value U_{22}[C(30)] 0.20(1) $Å^2$, last mean shift/error 0.06.

1c: 388 variables, final R and R_w factors were 0.052 and 0.050, final residual density was 0.46 $eÅ^{-3}$ and a maximum thermal factor of 0.14(1) $Å^2$ for the U_{11}[C(33)], last mean shift/error 0.21.

1d: There are two t-butanol independent molecules, one of them appears two fold disordered with assigned populations of 0.50 each. 486 variables, the hydrogen atoms of the disordered groups being fixed at their calculated positions. Final R

TABLE 1.FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS AS IN :[a]

$$U_{eq} = (1/3)\cdot\sum(U_{ij}\cdot a^*_i\cdot a^*_j\cdot a_i\cdot a_j\cdot \mathrm{Cos}(\mathbf{a}_i,\mathbf{a}_j))$$

ATOM	x/a	y/b	z/c	$U_{eq}\cdot 10^4$
BR	0.12709(9)	0.13267(7)	0.20741(8)	682(4)
N1	-0.07919(53)	0.32570(43)	0.45132(52)	460(23)
N2	-0.09962(57)	0.24869(47)	0.50417(57)	520(24)
C3	-0.00504(67)	0.20463(53)	0.51092(64)	456(26)
N4	0.07245(49)	0.25067(42)	0.46065(50)	425(21)
N5	0.18474(49)	0.22212(41)	0.45338(57)	435(22)
C6	0.25912(62)	0.29896(52)	0.45442(63)	424(26)
C7	0.22451(59)	0.36179(56)	0.35953(64)	434(25)
S8	0.08437(18)	0.41182(14)	0.36451(19)	524(7)
C9	0.02361(62)	0.32694(53)	0.42626(58)	414(25)
C10	-0.16585(108)	0.39302(98)	0.42961(175)	763(57)
S11	0.02726(20)	0.10394(15)	0.56766(21)	611(8)
C12	-0.10846(117)	0.07908(106)	0.60495(175)	862(61)
C13	0.38004(62)	0.26862(50)	0.45294(63)	428(26)
C14	0.41096(74)	0.21919(61)	0.37082(77)	573(32)
C15	0.52402(85)	0.19383(76)	0.37088(99)	708(40)
C16	0.60583(86)	0.22010(71)	0.45173(102)	737(43)
C17	0.57547(91)	0.26983(81)	0.53370(110)	817(46)
C18	0.46212(87)	0.29250(72)	0.53559(98)	676(39)
C19	0.31141(66)	0.43806(56)	0.36951(67)	477(28)
O20	0.31604(51)	0.48617(42)	0.44530(50)	647(23)
C21	0.39272(66)	0.44369(48)	0.29081(70)	451(27)
C22	0.49980(75)	0.47878(58)	0.32661(87)	553(33)
C23	0.57819(95)	0.48732(74)	0.25871(108)	728(45)
C24	0.55220(111)	0.46253(77)	0.15358(110)	816(50)
C25	0.44726(116)	0.42757(69)	0.11904(101)	765(47)
C26	0.36681(86)	0.41666(58)	0.18644(71)	588(33)
O31	-0.13081(167)	0.07810(149)	0.27044(150)	2075(101)
C30	-0.17428(245)	0.15835(217)	0.25535(123)	2278(163)

[a] Compound 1a.

TABLE 2.FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS AS IN :[b]

$$U_{eq} = (1/3)\cdot\sum(U_{ij}\cdot a^*_i\cdot a^*_j\cdot a_i\cdot a_j\cdot \mathrm{Cos}(\mathbf{a}_i,\mathbf{a}_j))$$

Atom	x/a	y/b	z/c	$U_{eq}\cdot 10^4$
BR	0.13706(4)	0.13538(3)	0.21051(4)	683(2)
N1	-0.07090(24)	0.32658(20)	0.46102(25)	458(10)
N2	-0.09256(26)	0.25037(21)	0.51373(26)	493(10)
C3	0.00077(29)	0.20525(23)	0.51597(28)	430(11)
N4	0.07704(22)	0.24906(18)	0.46536(22)	389(8)
N5	0.18715(23)	0.21977(19)	0.45562(25)	408(9)
C6	0.26166(28)	0.29682(23)	0.45667(28)	404(10)
C7	0.22926(28)	0.35961(23)	0.36347(28)	406(10)
S8	0.09027(8)	0.40830(6)	0.36789(8)	496(3)
C9	0.03059(27)	0.32599(23)	0.43251(26)	399(10)
C10	-0.15606(45)	0.39510(36)	0.44167(61)	754(21)
S11	0.03123(9)	0.10407(7)	0.57173(9)	553(3)
C12	-0.10162(47)	0.07983(42)	0.61570(54)	704(20)
C13	0.38161(29)	0.26676(24)	0.45634(30)	459(11)
C14	0.41479(34)	0.21425(29)	0.37838(38)	562(14)
C15	0.52644(39)	0.19153(37)	0.37914(52)	741(19)
C16	0.60391(45)	0.22097(46)	0.45558(63)	900(26)
C17	0.57200(46)	0.27331(47)	0.53185(64)	924(24)
C18	0.46089(39)	0.29576(33)	0.53375(44)	667(16)
C19	0.31517(29)	0.43610(22)	0.37184(28)	418(10)
O20	0.31724(24)	0.48484(19)	0.44431(23)	584(9)
C21	0.39877(31)	0.43949(22)	0.29701(29)	453(11)
C22	0.50245(36)	0.47657(28)	0.32993(40)	586(15)
C23	0.58172(47)	0.48578(36)	0.26126(52)	768(21)
C24	0.55718(52)	0.45983(36)	0.16029(54)	848(23)
C25	0.45452(54)	0.42356(37)	0.12656(46)	817(21)
C26	0.37512(44)	0.41255(29)	0.19443(35)	615(15)
C30	-0.18097(74)	0.19285(85)	0.24859(71)	1283(43)
*O31	-0.08542(61)	0.23170(45)	0.26342(50)	746(29)
C32	-0.17813(94)	0.10565(60)	0.29808(79)	1242(39)
*O33	-0.12515(79)	0.05710(60)	0.24904(99)	1052(47)

(*) means population parameters of 0.52(2) and 0.48(2) respectively

[b] Compound 1b.

TABLE 3.FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS AS IN : [a]

$U_{eq}=(1/3).\sum(U_{ij}.a^*_i.a^*_j.a_i.a_j.\mathrm{Cos}(a_i,a_j))$

ATOM	x/a	y/b	z/c	$U_{eq}.10^4$
BR	0.08881(3)	0.88230(5)	0.35506(3)	63X(2)
N1	0.15907(20)	0.72391(33)	0.57867(19)	455(14)
N2	0.13526(22)	0.80081(34)	0.61603(20)	490(15)
C3	0.07500(25)	0.82907(38)	0.57779(23)	420(16)
N4	0.06142(20)	0.77396(31)	0.51825(18)	413(13)
N5	0.00073(22)	0.78305(37)	0.46605(22)	444(15)
C6	-0.01921(24)	0.67329(40)	0.43763(23)	395(16)
C7	0.03406(25)	0.62135(45)	0.40644(24)	418(15)
S8	0.12323(6)	0.61792(11)	0.45965(6)	474(4)
C9	0.11539(24)	0.70846(38)	0.52029(23)	410(16)
C10	0.22721(34)	0.67726(70)	0.60344(44)	696(27)
S11	0.01812(7)	0.92233(10)	0.59619(6)	462(4)
C12	0.06702(47)	0.95654(69)	0.67922(32)	758(30)
C13	-0.08753(24)	0.68086(40)	0.38661(23)	427(16)
C14	-0.09391(29)	0.73728(46)	0.32676(26)	535(19)
C15	-0.15629(30)	0.74005(55)	0.27869(30)	632(22)
C16	-0.21201(33)	0.68667(57)	0.28969(33)	672(24)
C17	-0.20681(28)	0.63138(55)	0.34852(31)	618(22)
C18	-0.14521(27)	0.62899(51)	0.39660(29)	554(20)
C19	0.01963(25)	0.50108(39)	0.38921(22)	426(16)
O20	-0.02046(20)	0.45022(29)	0.41383(18)	566(14)
C21	0.05691(26)	0.44743(40)	0.34607(23)	447(17)
C22	0.06273(35)	0.33389(51)	0.34840(33)	639(23)
C23	0.09658(43)	0.28010(69)	0.30859(42)	831(32)
C24	0.12225(39)	0.33745(69)	0.26379(37)	779(29)
C25	0.11747(34)	0.44876(65)	0.26125(32)	679(26)
C26	0.08594(29)	0.50466(52)	0.30290(26)	532(20)
O31	0.19216(27)	0.93673(40)	0.50274(25)	878(20)
C30	0.17966(44)	1.03921(59)	0.52797(37)	819(31)
C32	0.22699(60)	1.05122(112)	0.59532(53)	1019(44)
C33	0.17913(73)	1.12933(103)	0.48064(62)	1090(51)

[a] Compound **1c**.

TABLE 4.FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS AS IN : **1d**

$U_{eq}=(1/3).\sum(U_{ij}.a^*_i.a^*_j.a_i.a_j.\mathrm{Cos}(\underline{a}_i,\underline{a}_j))$

ATOM	x/a	y/b	z/c	$U_{eq}.10^4$
BR	0.26661(3)	0.15291(3)	0.16717(4)	688(2)
N1	0.11335(20)	-0.15861(17)	0.24655(26)	518(9)
N2	0.21902(21)	-0.19910(17)	0.32846(26)	527(9)
C3	0.28457(22)	-0.12786(18)	0.41611(27)	447(9)
N4	0.22521(18)	-0.04512(15)	0.38789(22)	428(7)
N5	0.26827(20)	0.04407(16)	0.46692(28)	470(9)
C6	0.17134(24)	0.09281(19)	0.49096(30)	461(10)
C7	0.06971(24)	0.11682(19)	0.34815(31)	477(10)
S8	0.00208(6)	0.01081(5)	0.21947(8)	563(3)
C9	0.11644(23)	-0.06625(19)	0.28385(28)	461(9)
C10	0.01889(33)	-0.21648(30)	0.13340(46)	826(15)
S11	0.42541(6)	-0.12892(5)	0.55289(8)	528(3)
C12	0.44707(36)	-0.25400(29)	0.53210(62)	995(20)
C13	0.22530(24)	0.18132(19)	0.59222(30)	484(10)
C14	0.27293(31)	0.25660(22)	0.55085(35)	604(12)
C15	0.23538(32)	0.18454(25)	0.73457(37)	646(14)
C16	0.33664(39)	0.33746(28)	0.78886(45)	796(17)
C17	0.29123(41)	0.26220(31)	0.83105(42)	813(18)
C18	0.32750(36)	0.33493(24)	0.64836(43)	721(15)
C19	-0.02775(25)	0.16397(21)	0.38556(32)	524(11)
O20	-0.07920(22)	0.11777(17)	0.44073(30)	710(11)
C21	-0.05350(26)	0.26507(21)	0.36095(32)	539(11)
C22	-0.00777(32)	0.31772(25)	0.28411(42)	686(14)
C23	-0.03788(43)	0.41195(31)	0.26400(59)	921(21)
C24	-0.11180(51)	0.45364(31)	0.31958(65)	1009(24)
C25	-0.15583(54)	0.40353(36)	0.39572(64)	1043(26)
C26	-0.12838(40)	0.30990(29)	0.41678(48)	808(18)
C30	0.33872(30)	-0.12770(27)	0.03218(40)	686(14)
O31	0.22938(25)	-0.09427(23)	0.03636(44)	1002(16)
C32	0.35415(52)	-0.08876(58)	-0.09322(56)	1221(28)
C33	0.44044(36)	-0.09438(36)	0.17157(46)	865(17)
C34	0.32332(48)	-0.23487(38)	0.01918(69)	1087(25)
C35	0.28396(58)	0.46163(30)	0.19745(48)	994(25)
*O36	0.27361(86)	0.38087(47)	0.27593(85)	1127(42)
*C37	0.41881(135)	0.43776(127)	0.19041(171)	1096(62)
*C38	0.20048(130)	0.45820(117)	0.05892(125)	1146(59)
*C39	0.29713(215)	0.54375(84)	0.30320(152)	1682(109)
*O46	0.18261(87)	0.39454(71)	0.10199(131)	1363(50)
*C47	0.30790(124)	0.45615(85)	0.34176(110)	1110(56)
*C48	0.18898(155)	0.55992(87)	0.16444(190)	1379(81)
*C49	0.35877(243)	0.67297(220)	0.14560(355)	1928(176)

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* Means population parameters = 0.50

and R_w were 0.042 and 0.047, and final residual density 0.38 eÅ^{-3} and maximum thermal factors of U_{11} C(39) 0.33(2) Å^2, last mean shift/error 0.15.

The scattering factors were taken from the International Tables[6]. All the calculations were performed on a VAX11/750 computer.

Results. Final atomic coordinates for the nonhydrogen atoms are given in Tables 1, 2, 3 and 4, according to the numbering given in Fig. 1 and being the same for all four compounds[7].

Results and Discussion.- Stoichiometry of the inclusion compounds. The proton n.m.r. spectra show the superimposed patterns of heterocycle 1[3] and the corresponding alcohol. The integral leaves no doubt that the stoichiometry is 1:1 for 1a, 1b and 1c, but that 1d contains two molecules of t-butanol for each molecule of the heterocycle. The method is general and reliable and shows that the host guest ratio is 2:1 for dioxane[3] and tetrahydrofuran and 1:1 for fluoroethanol and methyl-t-butylketone.

Salient features of the thermal decomposition processes of compounds 1a-1d are given in Table 5. Compounds 1a-1c are stable up to c.a. 120°C and decompose through a well defined stage with a maximum decomposition rate at 140-150°C. Elimination of t-butanol from the less stable compound 1d takes place through a complex process with involved three overlapped stages. In the first stage between 45 and 72°C, a weight loss occurs corresponding to 1/3 mol of t-butanol per formula unit. The two final stages are overlapped with the decomposition point of the host molecule near 170°C. The weight loss at 168°C is slightly smaller than that expected for two molecules of t-butanol because the release of t-butanol is overlapped with the decomposition of 1, but under constant heating at 110°C the overall weight loss (24.18%) is close to the theoretical one (24.22%).

In all cases, the value obtained for ΔH by differential scanning calorimetry (DSC), is higher than the corresponding molar heat of vaporization[8]. In compound 1d the lower thermal stability, the complexity of the decomposition process and the low value of ΔH (12.4 kcal.mol^{-1}) could be explained by the presence of two different types of t-butanol molecules in the 1d crystal.

Host geometry.- The constitution of ligand 1 in all four crystals is the same as that of its previously reported structure with dioxane as crystallization solvent,

TABLE 5. Data on Thermal Decomposition of Compounds 1a-1d

Compound	Thermogravimetry			Differential Scanning Calorimetry	
	Temperature Range (°C)	Δm(%) Found	Required	DSC peaks[a] (°C)	ΔH Kcal. mol^{-1}
1a	117-160	6.48	6.46	149	13.6
1b	118-159	8.91	9.04	146	13.9
1c	123-162	11.88	11.47	140	17.3
1d	45-168	22.95	24.22	77, 90, 141	24.9[b]

[a] Endothermic processes

[b] Value for 2 molecules of the guest

Table 6. Selected geometrical parameters describing the cation (Å,°). The values corresponding to the DIOXANE containing compound are including for comparison purposes (1D).

	1D	1a	1b	1c	1d
C6-C7	1.536(4)	1.546(11)	1.558(5)	1.529(8)	1.547(4)
N5-C6	1.483(4)	1.462(10)	1.474(5)	1.479(7)	1.467(4)
C6-C7-S8	112.6(2)	111.8(5)	111.7(2)	115.8(3)	113.4(2)
S8-C7-C19	104.4(2)	106.6(5)	107.8(2)	102.6(3)	107.9(2)
C6-C7-C19	113.6(2)	107.2(6)	107.1(3)	112.7(4)	108.1(2)
S8-C7-C19-O20	104.4(3)	55.8(9)	54.0(4)	108.6(5)	59.6(3)
H6-C6-C7-H7	-171(3)	-163(6)	-176(4)	166(10)	-177(3)
H5-N5-C6-H6	174(4)	163(7)	172(4)	170(6)	168(3)

1D[3]. For instance, H(5) is cis with respect to H(7) and trans with respect to H(6), as shown in Fig. 1, and the positive charge is mainly located around N(1). However, the conformation of the host molecule is slightly different, as reflected by the values of the S(8)-C(7)-C(19)-O(20) torsion angles (Table 6). In 1c and 1D, O(20) is almost eclipsing C(6), with significantly different values of the two angles at C(7), S(8)-C(7)-C(19) < C(6)-C(7)-C(19). For these two compounds there is also a shortening of C(6)-C(7) and a lengthening of N(5)-C(6), with regard to the values measured in the other three compounds.

The geometrical characteristics of the alcohol molecules are gathered in Table 7 and will be discussed subsequently.

Table 7. Geometrical characteristics of the alcohol molecules (Å,°)

1a:	C30-O31	1.326(39)		
1b:	Br...O31-C31-C32	52.3(10)	O31-C30-H30A	115(7)
	S8v...O33-C32-C30	15.0(5)	O33-C32-C30	107.9(9)
	O31-C30-H30B	119(6)	O31-C30-C32	112.0(8)
	O33-C32-H32B	124(6)	O33-C32-H32A	91(9)
	C30-O31	1.284(12)	C32-O30	1.204(15)
	C30-C32	1.474(16)		
1c:	H31-O31-C30-H30	65(9)	O31-C30-H30	112(5)
	O31-C30-C33	113.2(7)	O31-C30-C32	107.7(7)
	C30-O31-H31	105(6)	C32-C30-C33	116.6(9)
	O31-C30	1.427(9)	O31-H31	1.20(12)
	C30-C32	1.484(12)	C30-C33	1.475(15)
1d:	H31-O31-C30-C32/C33	-68(4)/52(4)	O31-C30-C32	108.6(4)
	O31-C30-C33	109.4(4)	O31-C30-C34	103.9(4)
	C32-C30-C33	110.5(4)	C32-C30-C34	114.4(4)
	C33-C30-C34	109.9(4)	C30-O31-H31	105(4)
	C30-O31	1.438(5)	O31-H31	1.00(7)
	C30-C32	1.503(8)	C30-C33	1.496(5)
	C30-C34	1.505(7)		

No values are given for 1a as the hydrogen atoms could not be located. For the 1b compound the torsion angles are given with the Br and S8v atoms as it is supposed that the unlocalized H31 and H33 atoms are forming hydrogen bonds, see experimental part. In 1d case no values for the disordered molecule are given. (Symmetry operation v:-x,1/2+y,1/2-z)

Packing.- The overall packing characteristics are given in Table 8, where it can be noticed that going from 1a to 1d there is in the first three compounds a smooth change in density and thus, in its proportional number of atoms per Å^3, while the presence of 2 independent t-BuOH molecules gives in 1d a more swollen structure. This is also reflected in the amount of volume per alcohol molecule, which for the first three compounds gives an estimation of that volume, as close spheres, of about 20 Å^3 per atom (sequence 40, 60, 80 Å^3), whereas in 1d there is a change of about 30 Å^3.

Considering the main interatomic hydrogen contacts[9], around the bromide ion, Table 9, it can be noticed that it is fundamentally attached to one molecule of the heterocyclic cation through a Br...H(5)-N(5) bridge. On the other hand, the next nearest molecule (see symmetry operations in Table 9) displays contacts corresponding to different entourage of the bromide anion in different space groups, one type for the two pseudoisomorph $P2_{1/c}$ crystallizing compounds and another different type for the other two symmetry groups. The position of the alcohol molecules (only one of them in ethanol and t-butanol cases) is quite similar, in the four crystals, with respect to one host molecule (see Fig. 1). All this packing characteristics are intended to be described in the stereopairs of Figure 2.

Table 8. Lattice packing characteristics

	1a	1b	1c	1d
D x (gr.cm^{-3})	1.449	1.434	1.405	1.276
V (Å^3)	2266.2(3)	2359.5(1)	4948.3(2)	1591.8(1)
z	4	4	8	2
number of atoms in V	116	120	248	74
Number of atoms in the alcohol molecules in the unit cell	8 (4.2)	12 (4.3)	32 (8.4)	20 (10+10)* 2 (5+5)
Number of atoms × 10^2 per Å^3	5.119(1)	5.086(1)	5.012(1)	4.649(1)
V (Å^3) corresponding to one alcohol molecule	39.1(1)	59.0(1)	79.8(1)	107.6(1)

*Two independent t-BuOH molecules are present.

Alcohol geometries.- In order to compare X-ray results with those previously reported from theoretical and experimental values (cf. Table 10), the following points (apart of those due to the method itself) have to be considered: the thermal factors for methanol atoms are too high (see Table 1), the ethanol molecule appears disordered (see experimental part in Table 2) and the disordered t-butanol molecule have not been considered. Surprisingly enough only the X-ray structures (Table 10) of the two lowest melting point alcohols have been determined[10,11]. Table 10 shows the geometrical characteristics for those four alcohols.

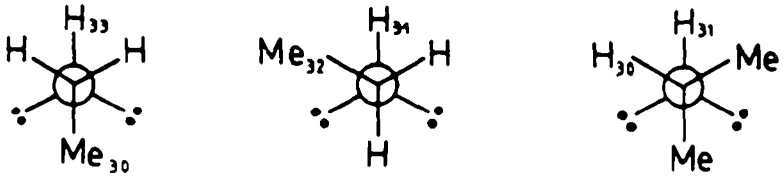
In the cases of methanol and ethanol the C-O bond length is clearly underestimated, however, the C-C bond length and the OCC angle in ethanol are in better agreement with literature values. On the other hand, the geometry of i-propanol is acceptable and that of t-butanol, which have not been previously determined, is in good agreement with theoretical calculations (Table 10).

Table 9. Selected common interatomic contacts (Å,°) of less than 4 Å, involving the Br$^-$ anion. Itallics refer to the bellow given symmetry operations, relating the second atom. Asterisk stands for the letter naming the hydrogen involved in the contact. Values for the Dioxane containing compound (1D) are included for comparison purposes.

Atoms	1D-i	1a-i	1b-i	1c-i	1d-i
Br...N5	3.486(3)	3.387(7)	3.427(3)	3.475(5)	3.506(3)
Br...H5	2.81(5)	2.35(11)	2.57(5)	2.78(7)	2.75(3)
Br...H5-N5	144(4)	161(8)	166(4)	155(6)	154(2)
Br...C7	3.469(3)	>4	>4	3.625(6)	3.630(4)
Br...H7	2.75(4)	3.33(6)	3.36(4)	2.90(20)	2.84(4)
Br...H7-C7	147(3)	132(5)	137(4)	118(11)	139(3)
Atoms	1D-ii	1a-ii	1b-ii	1c	1d
Br...C6	3.992(3)	3.907(8)	3.918(4)	>4	>4
Br...H6	3.13(3)	2.92(8)	3.05(5)	>4	>4
Br...H6-C6	152(2)	159(5)	148(3)	-	-
Atoms	1D-iii	1a-iii	1b-iii	1c-iv	1d-v
Br...C10$_*$	3.856(4)	>4	>4	3.657(7)	3.772(4)
Br...H10$_*$	2.93(6)B	3.14(13)C	2.27(8)C	3.38(8)A	2.95(5)C
Br...H10*-C10	161(5)	160(9)	157(5)	103(6)	148(4)

i: x,y,z; ii:x,1/2-y,z-1/2; iii:-x,y-1/2,1/2-z; iv: 1/2-x,3/2-y,1-z; v: -x,-y,-z; vi: -x,-y,1-z; vii: x,y,z-1

Alcohol conformations.- As the hydrogen atoms of the disordered ethanol molecule in compound 1b have not been located and since the Br...O(31)=3.188(7) Å, S_{8iii}...O(33)=2.787(11) Å distances (see Table 11) are less than the sum of the van der Waals radii (3.37 and 3.32 Å, respectively)[8], the following torsion angles have been calculated Br...O(31)-C(30)-C(32)=52.3(10)° and S_{8iii}...O(33)-C(32)-C(30)=15.0(5)°. These angles would suggest either a "gauche" conformation for both molecules of ethanol or an "eclipsed" one for the second (see, for example[12], ethanol solvate at 111 K , H-O-C-C=+6°). Theoretical calculations on the isolated ethanol molecule indicate that, generally, the "trans" conformer[13,14] is favoured, but a 4-31G calculation[15] concluded that both conformers differ only by 0.1 Kcal.mol^{-1}. It is worth of notice that crystals of pure ethanol[11] are 50:50 mixtures of "trans" and "gauche" forms.



EtOH "trans" EtOH "gauche" iPrOH "gauche"

Scheme 2

TABLE 10. Geometrical comparison of the alcohol molecule structures (Å,°)

Alcohol	This Work (Tabla 7)	X-Ray (pure compound)	Experimental (microwave)	Theoretical
Metanol a m.p. 175 K	C-0: 1.33(4)	C-0: 1.42(3)[b]	C-0: 1.425(2)[d]	C-0: 1.429[g]
Etanol b m.p. 156 K	C-0: 1.20(2)-1.28(1) C-C: 1.47(2) OCC: 112(1)-108(1) torsion: 52.3(10) torsion: 15.0(5)	C-0(t): 1.431(2)[c] C-0(g): 1.422(2) C-C(t): 1.499(3) C-C(g): 1.512(3) <OCC(t): 108.8(2) <OCC(g): 112.0(2) torsion(t): 179(3) torsion(g): 63(3)	C-0(t): 1.425(2)[e] C-0(g): 1.427(6) C-C(t): 1.530(2) C-C(g): 1.530(2) <OCC(t): 107.2(1) <OCC(g): 112.2(3) torsion(t): 180 torsion(g): 54(6)	C-0(t): 1.451[h] C-0(g): 1.452 C-C(t): 1.533 C-C(g): 1.526 <OCC(t): 106.3 <OCC(g): 111.7 torsion(t): 180.0 torsion(g): 61.5
i-Propanol c m.p. 184 k	C-0: 1.427(9) C-C: 1.475(15)-1.484(12) <OCC: 107.7(7)-113.2(7) <CCC: 116.6(9) torsion: 65(9)		C-0: 1.434[f] C-C: 1.523 <OCC: 110.9 <CCC: 112.3	C-0(t): 1.550[i] C-0(g): 1.555 C-C(t): 1.549 C-C(g): 1.550 <OCC(t): 110.9; <OCC(g): 112.8 <CCC(t): 113.0; <CCC(g): 113.0 torsion(t): 179.9 torsion(g): 61.4
t-Butanol d m.p. 298 k	C-0: 1.438(5)[a] C-C: 1.496(5)-1.505(7) <OCC: 103.9(4)-109.4(3) <CCC: 109.9(4)-114.4(4) torsion: 52(4)-68(4)			C-0: 1.441[j] C-C: 1.550-1.555 <OCC: 110.5 <CCC: 110.0 torsion: 60

[a]The disordered molecule has not been considered; [b]Ref. 10; [c]:Ref. 11; [d]Refs. 13, 14; [e]Ref 14; [f]Ref. 13; [g]4-31G, Refs. 14, 27; [h]4-21G, Refs. 15, 30; [i]MNDO, Ref. 13; [j]STO-3G, Refs. 13, 31.

Romanowski et al.[13] summarized the experimental and theoretical evidence concerning the i-propanol molecule, concluding that both "trans" and "gauche" forms exist in the gas phase, the latter being the most stable. In 1c crystal, only this conformer is present (Table 10)

Finally, t-butanol is in a staggered conformation (averaged torsion angle, 60°) in agreement with theoretical calculations. The t-butyl tilt, the angle between the local C_{3v} axis and the C(30)-O(31) bond, is 3.4(3)° comparable with the methanol methyl tilt, 3.26° (microwave[16]), 2.89° (theoretical calculation[14]).

Table 11. Selected common OH contacts (Å,°) of less than 4 Å. Symmmetry operations correspond to those of Table 9. Asterisk stands for that in 1b the hydroxyle involved is 033 instead of the 031 referred in the Table for the other compounds.

a.-Basic unit	1a-i	1b-i	1c-i	1d-i
031...Br	3.376(21)	3.452(10)	3.297(5)	3.571(3)
H31...Br	-	-	2.12(12)	2.59(7)
031-H31...Br	-	-	165(9)	170(7)

Dioxane geometry and conformation.- Since in our preceding paper[3] the data on dioxane geometry and conformation were not discussed, a brief summary will be presented here. The values of Table 12 show a very good agreement between our results on 1D and literature data. This situation is probably related to the fact that dioxane molecules in 1D are placed at symmetry centers, which constrains it to adopt a chair conformation.

Table 12. Geometrical comparison of dioxane molecule structures (Å,°)

	Our work[a] 1D	X-Ray (pure compound)[b] Phase I (279K)	 Phase II (153K)	Experimental (electron diffraction)[c]
C-O	1.419(5)	1.425(2)	1.431(1)	1.423(3)
C-C	1.480(8)	1.478(3)	1.513(2)	1.523(5)
<OCC	111.2(3)	111.2(1)	110.9(1)	109.2(5)[d]
<COC	108.6(4)	109.0(2)	109.9(1)	112.4(5)[d]
torsion	57.8(4)	57.5(2)	57.2(1)	57.9(5)

[a] Ref. 3; [b] Ref. 32; [c] Refs. 19, 33, 34; [d] Theoretical calculations[35] lead to the conclusion that the angle is larger than the COC angle.

Concluding remarks.- The approach we advocate to study the molecular structure of compounds liquid at room temperature (or, for that matter, gases) requires:

i) A suitable guest molecule capable of forming inclusion compounds with a great variety of host molecules.

ii) A particular molecule which cocrystallizes with the guest.

iii) Suitable crystals excluding defects and twins.

iv) Finally, host molecules should not be disordered.

This series of exclusive conditions limits the scope of the method we propose. The molecule we have found seems to fulfill the first condition. So far, all the alcohols and ethers we have tried give crystalline compounds (2nd. condition) that are suitable for X-ray determination (3rd. condition). However, the fourth condition is not always fulfilled. In addition to the ethanol problem, tetrahydrofuran inclusion crystals are pseudoisomorphs with those of dioxane and thus , they correspond to a disordered structure.

However, the other experimental methods used to determinate the molecular structure of liquids also have some drawbacks, for instance, in the five guest molecules whose structures we have determined as inclusion compounds: i) the methanol structure has been determined only by microwave spectroscopy (Table 10), with nematic phase n.m.r. studies it has been possible to determine only the H-C-H angle of the methyl group[17]; ii) the ethanol structure has been determined only by microwave spectroscopy (Table 10), nematic phase n.m.r. studies afford only the rotation barrier[18]; iii) the only data on the isopropanol structure are the microwave results reported in Table 10; iv) nothing experimental was known about tert-butanol before structure 1d was determined; v) the dioxane structure has been determined only by gas electron diffraction[19] since its permanent dipole moment is zero, nematic n.m.r. studies have made possible the determination of the chair-chair interconversion barrier, but not of the geometry[20]. Finally, regarding the case of tetrahydrofuran, that is disordered in the lattice of our quest 1, neither with electron diffraction[21,22] microwave spectroscopy[23,24] nor n.m.r. in a nematic phase[25] was it possible to determine its geometry, but only to study its pseudorotation. Finally, X-ray crystallography at -170°C of the pure compound solved the problem[26].

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