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Host-Guest Chemistry. 2.[1] Amine Inclusion Compounds of 2-[*o*-(Triphenylphosphoranylidenamino)benzyliden]amino-1 *H*-2,3-dihydroindazol-3-one. X-Ray Structure of Its 1 : 1 : 1 Inclusion Complex with Isopropylamine and Water

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Abstract. The crystal and molecular structure is reported for the inclusion compound 2-[*o*-(triphenylphosphoranylidenamino)benzyliden]amino-1 *H*-2,3-dihydroindazol-3-one/isopropylamine/water **3b**. The crystal structure consists of discrete dimeric salt-like aggregates joined together by strong N^+-H...$^-$O-C hydrogen bonds between pairs of centrosymmetrically-related indazolonate anions and isopropylammonium cations. Six other inclusion compounds have been prepared and characterized by NMR [with propylamine (**3a**), with *tert*-butylamine (**3c**), with *sec*-butylamine (**3d**), with *tert*-pentylamine (**3e**), with 1-methylbutylamine (**3f**) and with *iso*- pentylamine (**3g**)]. Two different arrangements are found, both with the host being in the anionic form. The guests are either: (i) one protonated amine and one water molecule (**3b** and **3f**); or (ii) one protonated amine and the corresponding neutral amine (**3a**, **3c**, **3d**, **3e** and **3g**).

Key words: Iminophosphoranes, amine inclusion compounds, ^{13}C CPMAS NMR spectroscopy, salt-like crystalline aggregates, crystal structure.

Supplementary Data relating to this article (structure factors, thermal components, hydrogen parameters and bond distances and angles, and ^{13}C-NMR shifts) are deposited with the British Library at Boston Spa, Wetherby, West Yorkshire, U.K., as Supplementary Publication No. SUP 82155 (23 pages).

[1] For Part 1, see Reference [1].
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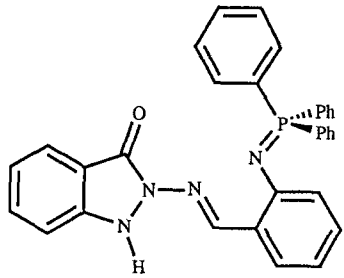

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1. Introduction

The title host **1** gives inclusion compounds with a wide variety of aliphatic alcohols (with methanol, **2a**; with ethanol, **2b**; with propanol, **2c**); the structure of the ethanol inclusion compound (**2b**) has been determined by X-ray crystallography [1]. To further explore its possibilities, we have decided to study the behaviour of **1** with regard to aliphatic amines.

2. Experimental

2.1. Sample Preparation

Host **1** was prepared as described previously [1]. Crystals of the inclusion compounds were obtained using the following procedure: a suspension of host **1** (0.5 g) in the appropriate amine (10 mL) was stirred at room temperature for 7 h. The solid was collected by filtration, washed with hexane (2 × 5 mL), air dried and recrystallized from the amine. With this procedure, crystals of **3b** ($1 \cdot C_3H_9N \cdot H_2O$) suitable for an X-ray study were obtained. Suitable single crystals could not be obtained with the other amines.

2.2. X-Ray Data of Compound 3b

Details of data collection and processing are presented in Table I. Several crystals were checked but all of them showed a mosaic spread wider than usual, although less than the scan width used. The structure was solved by Patterson and Dirdiff92 [2]. Hydrogen atoms were obtained from difference synthesis. The water molecule is disordered between three positions O(51), O(52) and O(53) with occupancy factors of 0.61(1), 0.24(1) and 0.15(1), respectively. The least populated position was refined isotropically. Calculations were performed on a VAX6410 computer using the XRAY80 System [3]. Scattering factors were obtained from the *International Tables for X-Ray Crystallography*, Vol. IV [4]. Fractional atomic coordinates and equivalent isotropic vibrational parameters for the non-hydrogen atoms are listed in Table II.

TABLE I. Crystal data and refinement parameters at room temperature.

Crystal data			
Chemical formula	$C_{32}H_{24}N_4OP^-\cdot C_3H_{10}N^+\cdot H_2O$		
M_r	589.7	Space group	Monoclinic, $P2_1/n$
a (Å)	31.0801(21)	$\alpha(^\circ)$	90
b (Å)	13.9617(5)	$\beta(^\circ)$	90.895(4)
c (Å)	8.5860(2)	$\gamma(^\circ)$	90
Z	4		
V (Å^3)	3725.3(3)	D_x(mg/m^3)	1.051
Radiation	CuK_α	No. of reflections for lattice parameters:	77
Wavelength (Å)	1.5418	θ range for lattice parameters (°)	2–45
Absorption coefficient (mm^{-1})	8.98	Temperature (K)	295
Crystal colour	Dark yellow	Crystal description	Prism
Crystal size (mm)	0.13 × 0.17 × 0.50		
Data collection			
Diffractometer type	Four circle Philips PW1100, bisecting geometry, graphite monocromator		
Collection method	$\omega/2\theta$ scans	Scan width	1.5°
No. of independent reflections	5542	θ_{max} (°)	60
No. of observed reflections	3470	No. standard reflections (interval)	2 (90 min.)
Criterion for observed	$I > 3\sigma(I)$	Variation of standards	9.5% decay
Refinement			
Treatment of hydrogen atoms	isotropic	Refinement: Least-Squares on F_o. 2-block matrix.	
R	0.095	No. of parameters refined	509*
wR	0.104	No. of reflections used in refinement	3470
Weighting scheme: Empirical as to give no trends in $\langle\omega\Delta^2F\rangle$ vs. $\langle\|F_{obs}\|\rangle$ and $\langle\sin\theta/\lambda\rangle$			
Max. thermal factor (Å^2)	$U22$[O(51)]=0.28(4)	$(\Delta\rho)_{max}$(e/Å^3)	0.69

* See experimental.

2.3. NMR Study in Solution and in the Solid State

The solution phase ($CDCl_3$ and DMSO-d_6) ^{1}H and ^{13}C spectra were recorded on a Bruker AC-200 (U. Murcia) spectrometer and the ^{13}C spectra in the solid state were recorded with a Bruker AC-200 (UNED) spectrometer using the standard

TABLE II. Final atomic coordinates and isotropic equivalent thermal factors, $U_{eq} \cdot 10^3$ (Å^2).

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
N(1)	0.1251(2)	−0.1302(4)	0.3745(6)	69(2)	C(22)	0.3196(3)	−0.1305(6)	0.4306(10)	101(3)
N(2)	0.0972(1)	−0.0679(3)	0.2945(5)	56(2)	C(23)	0.3416(3)	−0.0527(6)	0.4838(13)	111(4)
C(3)	0.0685(2)	−0.1122(4)	0.1980(7)	64(2)	C(24)	0.3196(2)	0.0231(5)	0.5502(11)	91(3)
C(3a)	0.0775(2)	−0.2106(5)	0.2151(7)	69(2)	C(25)	0.2804(2)	0.2236(4)	0.6210(6)	56(2)
C(4)	0.0607(3)	−0.2945(6)	0.1470(11)	101(3)	C(26)	0.2858(2)	0.2609(4)	0.4732(7)	71(2)
C(5)	0.0773(3)	−0.3811(6)	0.1888(12)	113(4)	C(27)	0.3128(3)	0.3386(5)	0.4496(9)	89(3)
C(6)	0.1122(3)	−0.3852(6)	0.2973(11)	110(3)	C(28)	0.3345(2)	0.3788(6)	0.5742(12)	95(3)
C(7)	0.1296(2)	−0.3052(5)	0.3608(9)	92(3)	C(29)	0.3293(3)	0.3439(6)	0.7192(12)	101(3)
C(7a)	0.1122(2)	−0.2156(5)	0.3234(7)	66(2)	C(30)	0.3023(2)	0.2668(5)	0.7456(7)	75(2)
O(8)	0.0403(1)	−0.0676(3)	0.1150(6)	89(2)	C(31)	0.2398(2)	0.0998(4)	0.8456(6)	52(2)
N(9)	0.0988(1)	0.0295(3)	0.3111(5)	58(2)	C(32)	0.2705(2)	0.0547(6)	0.9367(7)	81(2)
C(10)	0.1286(2)	0.0619(4)	0.4019(6)	55(2)	C(33)	0.2643(3)	0.0420(7)	1.0957(8)	98(3)
C(11)	0.1336(2)	0.1627(4)	0.4368(6)	56(2)	C(34)	0.2269(3)	0.0720(5)	1.1623(6)	77(2)
C(12)	0.1712(2)	0.1920(4)	0.5216(6)	55(2)	C(35)	0.1962(2)	0.1152(5)	1.0731(7)	80(2)
C(13)	0.1742(2)	0.2874(4)	0.5671(7)	68(2)	C(36)	0.2024(2)	0.1296(4)	0.9168(6)	67(2)
C(14)	0.1424(2)	0.3531(5)	0.5243(10)	85(3)	N(40)	0.0341(2)	0.1181(6)	0.0302(8)	77(2)
C(15)	0.1067(2)	0.3245(5)	0.4383(9)	86(3)	C(41)	0.0715(3)	0.1479(8)	−0.0690(12)	114(4)
C(16)	0.1024(2)	0.2306(5)	0.3988(8)	71(2)	C(42)	0.0767(4)	0.0766(10)	−0.1947(14)	146(5)
N(17)	0.2024(1)	0.1234(3)	0.5487(5)	60(1)	C(43)	0.0671(5)	0.2478(10)	−0.1176(21)	181(7)
P(18)	0.24582(4)	0.12138(9)	0.64079(14)	47(1)	O(50)*	−0.0008(4)	0.2690(7)	0.2401(15)	149(5)
C(19)	0.2755(2)	0.0213(4)	0.5638(6)	56(2)	O(51)*	−0.0212(10)	0.1423(31)	0.4078(34)	185(17)
C(20)	0.2538(2)	−0.0590(5)	0.5123(7)	73(2)	O(52)*	−0.0346(49)	0.4214(118)	0.2914(181)	293(51)
C(21)	0.2758(3)	−0.1349(5)	0.4453(9)	93(3)					

* pp[O(50)]=0.61(1), pp[O(51)]=0.24(1), pp[O(52)]=0.15(1).

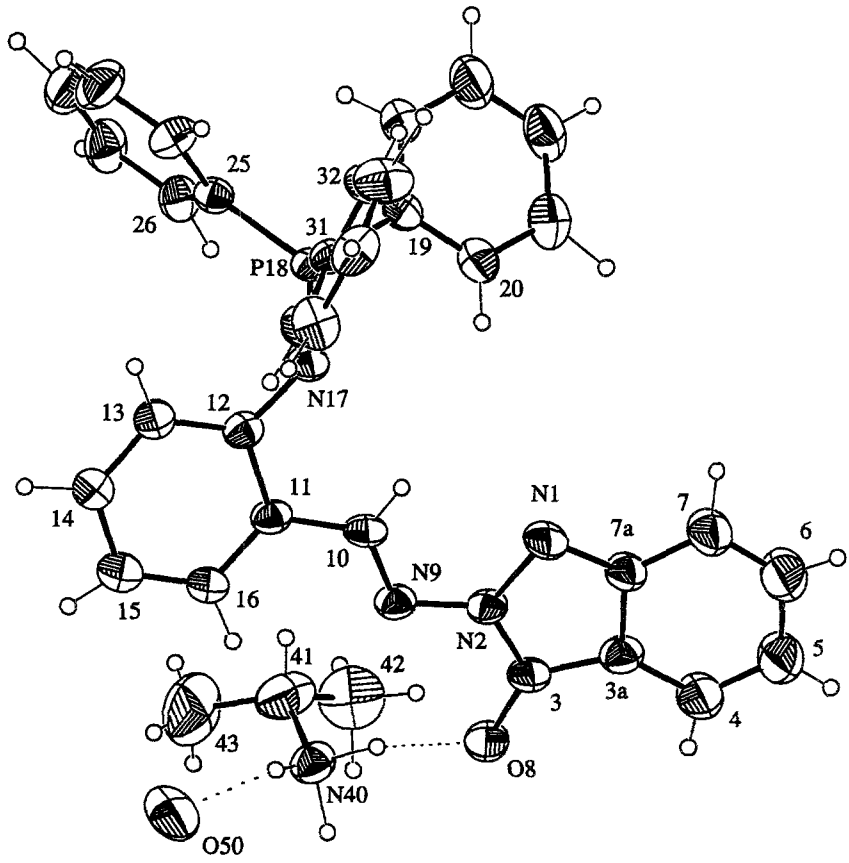


Fig. 1. ORTEP view of the asymmetric unit of complex **3b** showing the labelling scheme. The dashed lines denote hydrogen bonds.

conditions described in previous works [1, 5, 6]. The ^{1}H-NMR spectra were used only to determine the stoichiometry of the complexes and will not be discussed further.

3. Results and Discussion

Seven compounds were prepared from aliphatic primary amines with differently branched substituents including RCH_2NH_2 derivatives (propylamine, isopentylamine), $RR'CHNH_2$ derivatives (isopropylamine, *sec*-butylamine, 1-methylbutylamine) and $RR'R''CNH_2$ derivatives (*tert*-butylamine, *tert*-pentylamine). With isobutylamine a 2 : 1 complex was obtained but in insufficient amount to be fully characterized by solid-state NMR.

TABLE III. Selected geometrical parameters (Å,°).

	3b	Ref.[1]	*CSD⁻	#CSD	**5**	**4**
N(1)-N(2)	1.400(6)	1.425(2)	1.376	1.404	1.368	1.403
N(1)-C(7a)	1.330(8)	1.396(2)	1.332	1.384	1.356	1.445
N(2)-C(3)	1.357(7)	1.378(2)	1.367	1.365	1.446	1.458
C(3)-C(3a)	1.409(9)	1.444(3)	1.401	1.467	1.460	1.486
C(3a)-C(7a)	1.413(8)	1.381(2)	1.392	1.393	1.470	1.431
C(3)-O(8)	1.282(7)	1.236(2)	1.304	1.231	1.251	1.232
N(1)-N(2)-C(3)	114.3(5)	112.2(1)	112.9	112.7	112.1	109.8
N(2)-C(3)-C(3a)	104.7(5)	104.8(1)	105.6	103.9	104.4	106.0
C(3)-C(3a)-C(7a)	105.4(5)	107.7(1)	104.7	107.9	104.4	106.0
C(3a)-C(7a)-N(1)	113.3(6)	111.1(1)	113.6	109.2	111.5	110.1
C(7a)-N(1)-N(2)	102.4(4)	103.6(1)	103.2	105.9	106.9	106.8
N(2)-C(3)-O(8)	123.7(5)	125.0(2)	122.8	125.2	123.3	123.7
C(3a)-C(3)-O(8)	131.6(6)	130.1(2)	131.6	130.8	132.2	130.2

	3b		**3b**
N(2)-N(9)	1.367(7)	N(9)-C(10)	1.283(6)
C(10)-C(11)	1.447(8)	C(11)-C(12)	1.427(7)
C(12)-N(17)	1.381(7)	N(17)-P(18)	1.554(4)
N(40)-C(41)	1.510(11)	C(41)-C(42)	1.480(17)
C(41)-C(43)	1.461(18)		
N(2)-N(9)-C(10)	116.0(4)	N(9)-C(10)-C(11)	123.0(5)
C(10)-C(11)-C(16)	122.8(5)	C(10)-C(11)-C(12)	118.1(5)
C(11)-C(12)-N(17)	117.0(5)	C(13)-C(12)-N(17)	125.0(5)
C(12)-N(17)-P(18)	134.5(4)	N(40)-C(41)-C(42)	108.6(8)
N(40)-C(41)-C(43)	110.8(9)	C(42)-C(41)-C(43)	116.4(11)
N(1)-N(2)-N(9)-C(10)	2.0(7)	N(2)-N(9)-C(10)-C(11)	−177.5(5)
N(9)-C(10)-C(11)-C(16)	12.2(8)	C(10)-C(11)-C(12)-N(17)	7.2(7)
C(13)-C(12)-N(17)-P(18)	5.8(9)	C(12)-N(17)-P(18)-C(19)	−160.3(5)
C(12)-N(17)-P(18)-C(25)	−42.9(6)	C(12)-N(17)-P(18)-C(31)	82.9(5)

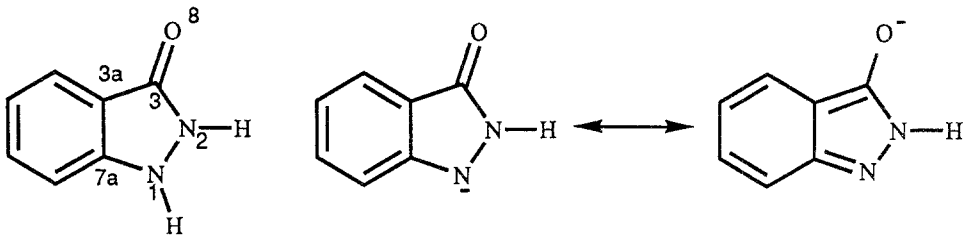
Intermolecular contacts:[a]

N(40)-H(401)···O(8)$_{(-x,-y,-z)}$	1.09(9)	2.699(9)	1.62(9)	173(7)
N(40)-H(402)···O(8)	1.11(10)	2.704(8)	1.64(10)	158(7)
N(40)-H(403)···O(50)	0.76(6)	2.987(14)	2.24(6)	171(5)

* (CSD refcode: BIVHIX).

(CSD refcodes: BOWMAB, CIGHOP, FADMIG, TNIZMS).

[a] Geometric parameters of each X-H···Y hydrogen bond are given in the order: X-H(Å), X···Y(Å), H···Y(Å) and X-H···Y(°).



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3.1. Molecular Structure and Packing of **3b**

The molecular structure and the atomic numbering scheme are shown in Figure 1. The main differences between compound **3b** and the free host **1** and its ethanol inclusion compound **2b** [1] are the different patterns of bond distances and angles in the five-membered ring of the indazolinone skeleton and the conformation around the P-N bond [perpendicular vs. parallel (C-N-P-C: −30, 90, −150° vs. ±60, 180°)].

For comparison purposes, Table III contains a selection of molecular dimensions of compound **3b** together with the averaged geometry for host **1** and compound **2b** and a literature survey performed via the Cambridge Structural Database (April 1993 release) [7] on related molecules (CSD^- and CSD stand for the anion and the neutral molecule, respectively). The results of the AM1 semiempirical geometry optimization (MOPAC 6.0) [8] for the indazolinone moiety **4** and its anion **5** are also included.

The similarities between **1**, **2b** and CSD, on the one hand, and between **3b** and CSD^-, on the other, are clearly apparent; shortening of the N(1)-C(7a), N(1)-N(2) and C(3)-C(3a) and lengthening of the C(3a)-C(7a) and C(3)-C(8) bonds. These differences are also apparent in the semiempirical calculated geometries for **4**, which corresponds to CSD, and for **5**, which corresponds to CSD^- (see Table III). The indazolinone anion system of **3b** is planar within experimental errors, in contrast with the lack of planarity of **1** and **2b**. Moreover, the N(1) atom is surrounded in the crystal by phenyl rings of other molecules (Figure 2 and Table III) and directed away from the O = C bond with the concomitant loss of the N-H...O = C intermolecular hydrogen bond, previously observed in compounds **1** and **2b** [1].

In compound **3b** intermolecular hydrogen bonds, involving the guest, link pairs of isopropylammonium cations, indazolinone anions and water molecules to form a cyclic dimeric unit around each symmetry center (Figure 2 and Table III).

For the characterization of the shape and size of the guest, a model of interpenetrating spheres of van der Waals radii was used. The isopropylammonium cation can be described as an oblate spheroid ($Q_{ij}^2 = i_{ij}^v / i_{ij}^s = 0.67, 0.67, 0.56$) of 3.09,

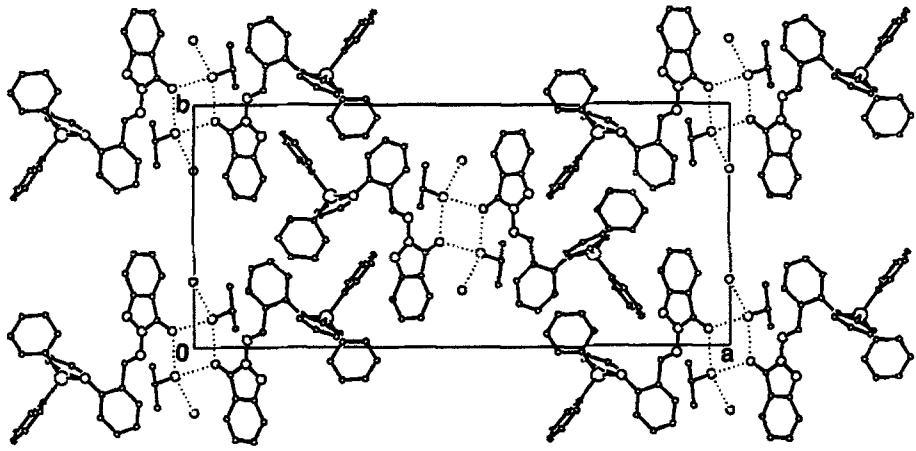


Fig. 2. Crystal structure viewed along the *c* axis showing the packing of centrosymmetric dimeric units. The disordered water molecule is shown in its most populated site. Hydrogen bonds are indicated by broken lines.

3.17 and 2.45 Å axis ($S = 99.4$ Å^2, $V = 68.9$ Å^3) where i^v_{ij} and i^s_{ij} are the specific planar moments of volume and surface [9]. The disordered water molecules are located on a network of interconnected channels, irregular in shape, along the *b* and *c* axes and centered at $x = 0$ and 1/2. Two sections of these channels are represented in Figure 3.

3.2. NMR Study

Solution phase ^{1}H NMR spectra and analytical data were used to determine the stoichiometries of the seven complexes **3a–3g** prepared from the corresponding amines **6a–6g** (Table IV).

Since the X-ray study of compound **3b** showed that the host was in its anionic form, **3b**$^-$, by loss of the N-H proton, and the amine **6b** in its cationic form, **6bH**$^+$, and since no other suitable single crystals were obtained, ^{13}C-NMR spectroscopy was used to determine whether the remaining compounds were also salts. The results are reported in Tables V (amines) and VI (host, see Supplementary Material).

Although amine chemical shifts have been reported in the literature (see, for instance, ref. [10]) we have redetermined them in DMSO-d_6. The salts corresponding to these amines, in the form of hydrochlorides, were recorded in the same solvent and the difference in chemical shifts, $\Delta\delta^b$, calculated. These differences correspond to the 'protonation induced shifts' (PIS) [11, 12]. The spectrum of the complex was determined in $CDCl_3$ solution: the signals corresponding to the host were always the same and identical to those already published [1]. The signals of the amines were shifted with regard to the neutral amine; we have checked that the shift, $\Delta\delta^c$, is not a solvent effect by recording the spectra of all the amines in $CDCl_3$

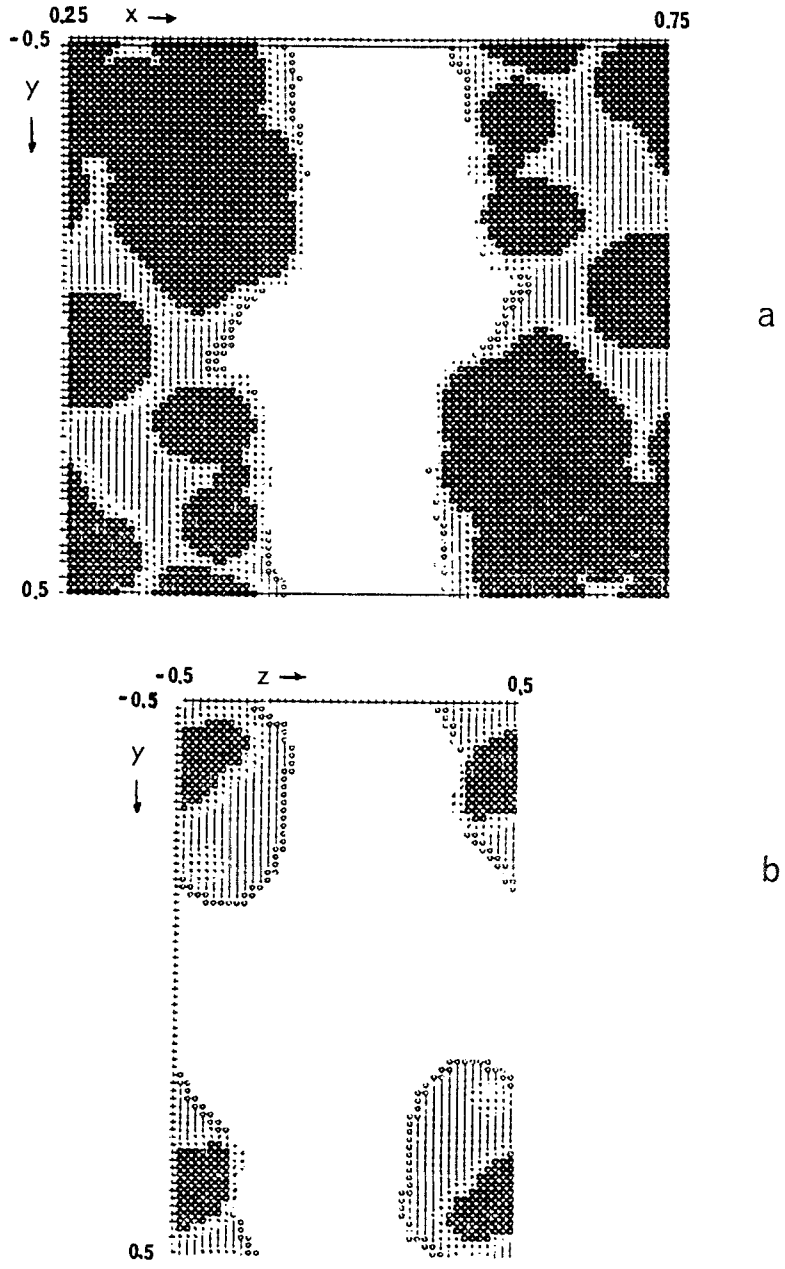
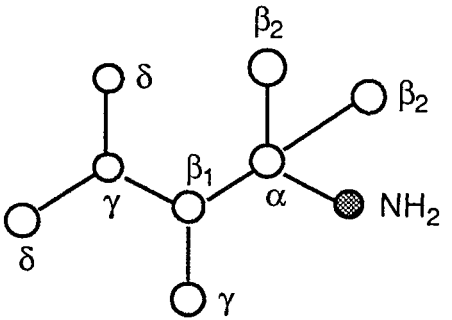


Fig. 3. Two perpendicular sections, (a) through $z = 0$ and (b) $x = 1/2$, of the channels that hold the disordered water molecules. A 0.2 Å grid for the search of the voids was used and the molecular surface was smoothed by rolling a sphere of radius 1.4 Å. The clefts are drawn in grey while the interior of atoms appears dark.

TABLE IV. Amine inclusion compounds **3a–3h**.



Guest Amine	IUPAC name	Trivial name	Guest/host stoichio-metry	H_2O of cryst.	α	β	γ	δ	Yield (%) in comp. **3**	Appearance of comp. **3**	M.P. (°C) of comp. **3**	Molecular formulae[d]
6a	Propyl	Propyl	2 : 1	No	1	1	1	0	75	orange prisms	124–125	$C_{38}H_{43}N_6OP$
6b	1-Methylethyl	Isopropyl	1 : 1	Yes	1	2[a]	0	0	84	yellow prisms	145–146	$C_{35}H_{36}N_5O_2P$
6c	1,1-Dimethylethyl	*Tert*butyl	2 : 1	No	1	3[a]	0	0	91	yellow prisms	132–133	$C_{40}H_{47}N_6OP$
6d	1-Methylpropyl	*Sec*butyl	2 : 1	No	1	2[b]	1	0	76	orange prisms	102–103	$C_{40}H_{47}N_6OP$
6e	1,1-Dimethylpropyl	*Tert*pentyl	2 : 1	No	1	3[c]	1	0	62	yellow prisms	119–120	$C_{42}H_{51}N_6OP$
6f	1-Methylbutyl	------	1 : 1	Yes	1	2[b]	1	1	60	orange prisms	110–111	$C_{37}H_{40}N_5O_2P$
6g	3-Methylbutyl	Isopentyl	2 : 1	No	1	1	1	2[a]	50	orange prisms	109–110	$C_{42}H_{51}N_6OP$

[a] Identical.

[b] Different.

[c] Two identical, one different.

[d] Correct microanalyses (C,H,N,±0.4%) corresponding to the formulae of compounds **3a–3g**.

(not reported). The value of $\Delta\delta^c$ is, in general, similar in sign to $\Delta\delta^b$ but smaller in absolute value: in solution the signal of the amine is averaged between the neutral and the protonated form. But even in the case when there is only one amine (**3b**, **3f**) the small $|\Delta\delta^c|$ values indicate that the salts $Host^-$ RNH_3^+ are dissociated due to the weak acid character of the 2-substituted indazolinones. A relationship exists between both $\Delta\delta$ values: $\Delta\delta^c = 0.27 + 0.181\ \Delta\delta^b$ ($R = 0.91$), and the slope, 0.181, corresponds to the attenuation due to partial protonation.

In the solid state, one protonated guest amine (**3b** and **3f**) or one protonated and one neutral guest amine (all other cases) are observed [Table V, (P) and (N), respectively]. The difference in their chemical shifts, $\Delta\delta^d$, is similar to $\Delta\delta^b$, which is clear proof of the common structure of all these compounds. Here also a rough linear relationship exists: $\Delta\delta^d = -0.68 + 0.964\ \Delta\delta^b$ ($R = 0.91$), but now the slope is near unity. In some cases (**3b**, **3g**) the signal corresponding to a methyl group in the cation is split into two signals, probably due to conformational differences in the crystal.

We have reported the signals of the host in the seven complexes in Table VI (see Supplementary Material). The first observation is that all are remarkably alike considering the crystal packing effects. If the averaged value in compounds **3a**–**3g** is compared with the signals of pure host [1], then the differences, $\Delta\delta$, are only significant (> 1.4 ppm) on carbons C(3), C(3a), C(4) and C(5). These effects correspond to the transformation of indazolone **4** into the indazolonate anion **5**.

4. Conclusions

In conclusion, host **1** has proved to yield inclusion compounds with n-alkanols (CH_3OH, C_2H_5OH, C_3H_7OH) and with primary amines (linear or branched). In the first case, they are classical host-guest compounds. In the second one, the structures reported here for compounds **3** are related to Weber's 'salt-like crystalline aggregate' or 'crystalline salt-type associate' [13–15], the main difference being that the examples reported by Weber concern naphthoic acids and aromatic heterocycles (imidazole, pyridine) whereas in our case the acid is much weaker (it is an N-H acid) and the base is a saturated amine. In all cases there is a second neutral molecule, either water or an amine. There are some structures which contain both a base and its conjugated acid, for instance, benzimidazole and the benzimidazolium cation (CSD refcode: BZIMBF10) [16].

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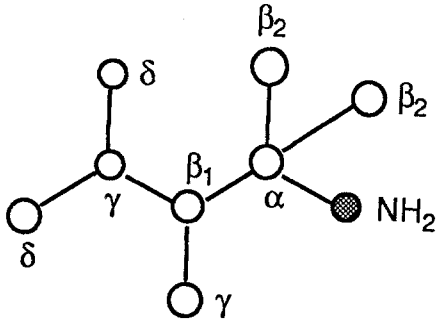
TABLE V. ^{13}C NMR spectroscopy of amines **6a–6g** and their corresponding inclusion compounds **3a–3g**.



Compound	Solvent	α	β_1	β_2	γ	δ
6a	DMSO-d_6	43.78	26.58	—	11.09	—
6aH^{+a}	DMSO-d_6	40.7	20.5	—	11.3	—
	$\Delta\delta^b$	−3.08	−6.08	—	0.21	—
3a	$CDCl_3$	43.11	25.13	—	11.04	—
	$\Delta\delta^c$	−0.67	−1.45	—	−0.05	—
	CPMAS(N)	44.74	29.20	—	10.34	—
	CPMAS(P)	41.90	20.93	—	10.34	—
	$\Delta\delta^d$	−2.84	−8.27	—	0.00	—
6d	DMSO-d_6	42.20	—	26.00	—	—
6bH^{+a}	DMSO-d_6	43.35	—	20.5	—	—
	$\Delta\delta^b$	1.15	—	−5.5	—	—
3b	$CDCl_3$	42.73	—	25.34	—	—
	$\Delta\delta^c$	0.53	—	−0.66	—	—
	CPMAS(P)	44.05	—	20.83[e]	—	—
	CPMAS(P)	—	—	21.75[e]	—	—
6c	DMSO-d_6	46.98	—	32.56	—	—
6cH^{+a}	DMSO-d_6	51.7	—	27.3	—	—
	$\Delta\delta^b$	4.72	—	−5.26	—	—
3c	$CDCl_3$	47.80	—	31.93	—	—
	$\Delta\delta^c$	0.82	—	−0.63	—	—
	CPMAS(N)	46.75	—	32.52	—	—
	CPMAS(P)	51.22	—	27.81	—	—
	$\Delta\delta^d$	4.47	—	−4.71	—	—
6d	DMSO-d_6	47.98	32.55	23.40	10.38	—
6dH^{+a}	DMSO-d_6	48.19	26.98	17.49	9.76	—
	$\Delta\delta^b$	0.21	−5.57	−5.91	−0.62	—
3d	$CDCl_3$	48.51	31.80	22.27	10.49	—
	$\Delta\delta^c$	0.68	−0.47	−0.58	0.50	—

TABLE V. Continued.

Compound	Solvent	α	β_1	β_2	γ	δ
	CPMAS(N)	47.82	31.48	23.13	10.24	—
	CPMAS(P)	48.76	27.51	16.73	10.24	—
	$\Delta\delta$[d]	0.94	−3.97	−6.40	0.00	—
6e	DMSO-d_6	48.91	36.97	29.78	8.58	—
6eH^{+}[a]	DMSO-d_6	53.91	32.33	24.29	7.92	—
	$\Delta\delta$[b]	5.00	−4.64	−5.49	−0.66	—
3e	$CDCl_3$	50.11	36.84	29.11	8.60	—
	$\Delta\delta$[c]	1.20	−0.13	−0.67	0.02	—
	CPMAS(N)	50.46	36.80	27.77	10.02	—
	CPMAS(P)	53.50	27.77	24.33	8.07	—
	$\Delta\delta$[d]	3.04	−9.03	−3.44	−1.95	—
6f	DMSO-d_6	46.13	42.32	23.91	19.10	13.87
6fH^{+}[a]	DMSO-d_6	46.55	36.17	18.02	18.16	13.71
	$\Delta\delta$[b]	0.42	−6.15	−5.89	−0.94	−0.16
3f	$CDCl_3$	46.85	41.33	22.81	19.36	13.98
	$\Delta\delta$[c]	0.72	−0.99	−1.10	0.26	0.11
	CPMAS(P)	48.41	31.17	19.00	19.00	14.90
6g	DMSO-d_6	39.82	42.90	—	25.12	22.46
6gH^{+}[a]	DMSO-d_6	37.06	35.62	—	25.01	22.14
	$\Delta\delta$[b]	−2.76	−7.28	—	−0.11	−0.32
3g	$CDCl_3$	39.64	41.92	—	25.53	22.31
	$\Delta\delta$[c]	−0.18	−0.98	—	0.41	−0.15
	CPMAS(N)	40.65	44.93	—	26.07	23.79
	CPMAS(P)	36.58	36.58	—	26.07	21.45[e]
	CPMAS(P)	—	—	—	—	19.62[f]
	$\Delta\delta$[d]	−4.07	−8.35	—	0.00	−3.26[e]

[a] Spectrum of the hydrochloride of the amine in DMSO-d_6.

[b] δ (ammonium chloride in DMSO-d_6) − δ (amine **6** in DMSO-d_6).

[c] δ (host-guest **3** in $CDCl_3$) − δ (guest **6** in DMSO-d_6).

[d] δ [CPMAS(P)] − δ [CPMAS(N)].

[e] The methyl groups of the protonated amine are split.

[f] Considering an average value for the methyl groups of the CPMAS(P) spectrum.

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