Unusual Host Properties. *X*-Ray Structures of Three Salt-like Crystalline Aggregates of 1,1′-Binaphthyl-8,8′-dicarboxylic Acid

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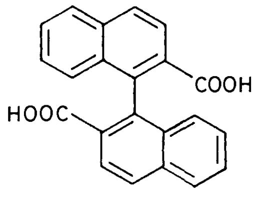
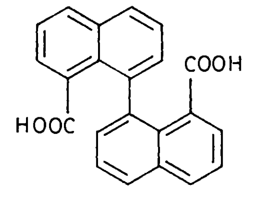
In contrast with 1,1′-binaphthyl-2,2′-dicarboxylic acid (**1**), isomeric 1,1′-binaphthyl-8,8′-dicarboxylic acid (**2**) does not form inclusion compounds with aprotic or proton-donor organic molecules. Instead, salt-like associations of (**2**) with basic components such as pyridine, derivatives of pyridine, or related heterocycles are readily obtained, and recrystallization of (**2**) from pyridine in the presence of other non-basic solvents, including cyclic ethers, dipolar aprotic compounds, and acids, gives crystalline ternary complexes. Crystal structures of the two-component aggregates (**2**)·pyridine (1 : 1) and (**2**)·3-(hydroxymethyl)pyridine, (1 : 1) and of the ternary crystal aggregate of (**2**)·pyridine·acetic acid (1 : 1 : 1) have been studied by *X*-ray diffraction. In the crystals of (**2**)·pyridine (1 : 1) and (**2**)·pyridine·acetic acid (1 : 1 : 1), the structures are built up from finite blocks of H-bonded (**2**)·pyridine and (**2**)·pyridine·acetic acid associations. In the case of (**2**)·3-(hydroxymethyl)pyridine (1 : 1) the side-chain hydroxy group of the pyridine moiety acts as a proton donor to the carboxyl group of a neighbouring molecule of (**2**), thus forming infinite undulating chains in the crystallographic *c*-direction. A characteristic feature of these structures is the intramolecular H bond between the carboxylic groups of (**2**), which works against the net bulkiness of the molecule and thus seems to result in the modest clathrate-forming ability of this host. Crystal data for (**2**)·pyridine (1 : 1): monoclinic ($P2_1$), $a = 8.080(1)$, $b = 17.254(2)$, $c = 7.715(1)$ Å, $\beta = 106.28(3)°$, $R = 0.049$ for 1 860 reflections; for (**2**)·3-(hydroxymethyl)pyridine (1 : 1): orthorhombic: (*Pbca*), $a = 15.426\,7(4)$, $b = 21.189\,5(6)$, $c = 13.372\,7(4)$ Å, $R = 0.049$ for 2 085 reflections; and for (**2**)·pyridine·acetic acid (1 : 1 : 1): triclinic ($P\bar{1}$), $a = 14.525(6)$, $b = 10.481(4)$, $c = 8.862(4)$ Å, $\alpha = 105.69(4)$, $\beta = 111.10(6)$, $\gamma = 86.37(6)°$, $R = 0.053$ for 2 686 observations.

1,1′-Binaphthyl-2,2′-dicarboxylic acid (2,2′-BNDA) (**1**) is a host molecule with superior inclusion and remarkable selectivity properties.[1–4] It belongs to the co-ordinatoclathrate type of hosts, which are characterized by the presence of a bulky skeleton and functional groups as basic requirements.[5] Geometric parameters of the host molecule, such as the position and orientation of the functional groups, are certainly also important,[1] but have not been scrutinized systematically. In order to study these dependencies we decided to investigate positional isomers of (**1**). Compound (**2**), 1,1′-binaphthyl-8,8′-dicarboxylic acid (8,8′-BNDA), is based on the same fundamental components as (**1**) but has different positions for the highly polar and co-ordinatively active carboxylic groups. Hence one may anticipate different packing in the crystal and thus modification of the inclusion behaviour.



(1)



(2)

Typical co-ordinatoclathrate hosts, such as 2,2′-BNDA (**1**),[1–4] but also many other carboxylic host molecules[6,7] with very different overall structures, readily form crystalline inclusions with a large number of small uncharged organic molecules, usually of polar nature, such as alcohols, carboxylic acids, amides, sulphoxides, or nitriles, but even in some cases with slightly non-polar compounds such as bromobenzene[3] or toluene.[1] In clear contrast to this behaviour, 8,8′-BNDA (**2**) did not allow the isolation of any analogous inclusion compound; it only yielded salt-type associations. On the other hand, these salt-like aggregates, with basic components such as pyridine, derivatives of pyridine, or other related heterocycles, all with 1 : 1 stoicheiometry, are obtainable easily on recrystallization from the respective amine solvent. Thus, the mono-salts of (**2**) with pyridine, 2-methylpyridine, 2-ethylpyridine, 3-(hydroxymethyl)pyridine, 2-(2-hydroxyethyl)pyridine, isochinoline, and pyrazine were obtained.

Unexpectedly, however, recrystallization of 8,8′-BNDA (**2**) from pyridine in the presence of other non-basic solvents, including cyclic ethers, dipolar aprotic compounds, and acids, gave specific crystalline ternary complexes, composed of (**2**), pyridine, and the non-basic solvent, as specified in Table 1. There is reason to suppose that a singular new type of clathrate compound was formed, where the virtual host species, an organic salt[8] or acid–base pair, has temporarily assembled on recrystallisation of the components. It seems possible that a change to other acid–base pairs involving (**2**) will alter the inclusion properties in a defined way. Most remarkable, however, is the fact that the formation of analogous ternary aggregates of (**2**), using the other cyclic amine solvents applied for salt-formation, failed completely under the same experimental conditions.

In order to find an explanation for the unusual inclusion properties of 8,8′-BNDA (**2**) and to define the mode of binding in its complexes, we studied the crystal structures of three compounds. These are the two-component aggregates of (**2**) with pyridine (1 : 1) and with 3-(hydroxymethyl)pyridine (1 : 1) and the ternary crystal aggregate of (**2**) with pyridine and acetic acid (1 : 1 : 1). Another stimulus for the structural studies is the possibility of relating the salt-type interactions, as assumed here, to possible binding modes of biotic complexes (enzyme–substrate complexes).[4,9] Previous investigations have revealed a close structural resemblance between the hydrated imidazolium complex of isomeric 2,2′-BNDA (**1**) and the native enzyme Streptomyces Griseus Protease A with reference to seven fitted atoms in the characteristic electrostatic pattern.[4]

Table 1. Ternary inclusion compounds of (**2**)·pyridine (1 : 1) [(**2**)·pyridine·X].

X	Stoicheiometric ratio[a]
Dioxane	1 : 1
Tetrahydrofuran	2 : 1
1,3-Dioxolane	2 : 1
Acetic acid	1 : 1
Propionic acid	1 : 1
Methacrylic acid	1 : 1
Acetone	2 : 1
Nitromethane	2 : 1
Dimethylformamide[b]	2 : 1

[a] Stoicheiometric ratio [(**2**)·pyridine] : X. [b] Solvents not included: methanol, ethanol, butan-1-ol, butan-2-ol, t-butyl alcohol, cyclopentanol, cyclohexanol, ethylene glycol, 1,2-propylene glycol, 2-methoxybutanol, 1-(*p*-chlorophenyl)ethanol, diethyl ether, ethyl vinyl ether, epichlorohydrin, acetaldehyde, propionaldehyde, cyclohexanone, formic acid, 2-chloropropionic acid, lactic acid, tartaric acid, benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene, bromobenzene, 2-aminotoluene, benzyl cyanide, chloroform, cyclohexane, dimethyl sulphoxide.

Results and Discussion

Views of the structures (**2**)·pyridine (1 : 1), (**2**)·3-(hydroxymethyl)pyridine (1 : 1), and (**2**)·pyridine·acetic acid (1 : 1 : 1) are presented in Figures 1(*a*)–(*c*) and 3(*a*)–(*c*). Figure 2 shows a fragment of the H-bonded heteromolecular aggregates formed in (**2**)·3-(hydroxymethyl)pyridine (1 : 1). The crystallographic numbering schemes of the atoms are displayed in Figures 1(*a*)–(*c*). Crystal data are given in Table 2. Atomic co-ordinates are listed in Table 3.

Molecular Structures.—The corresponding bond lengths and bond angles involving the non-hydrogen atoms of the naphthyl moieties of 8,8′-BNDA (**2**) agree well with each other, both in the two molecular halves and also in the three crystal structures studied. The present values are also in accordance with those published earlier for inclusion compounds of 2,2′-BNDA (**1**).[2,3] The molecular geometry is, however, different for these two binaphthyl derivatives. As seen in Figures 1(*a*)–(*c*), the positioning of the two carboxy groups of (**2**) results in a rather short intramolecular H bond between these groups (*cf.* Table 4). Consequently, the dihedral angle between the two naphthyl moieties decreases from a value of *ca.* 90° in (**1**)[2,3] to 64.61(6)° in (**2**)·pyridine (1 : 1), to 67.81(8)° in (**2**)·3-(hydroxymethyl)pyridine (1 : 1), and to 65.48(8)° in (**2**)·pyridine acetic acid (1 : 1 : 1); the inclination angles of the carboxy groups to the respective naphthyl planes in (**2**) [53.9(1)/57.0(3)° in (**2**)·pyridine (1 : 1), 61.1(2)/54.0(2)° in (**2**)·3-(hydroxymethyl)pyridine (1 : 1), and 54.6(2)/67.3(2)° in (**2**)·pyridine·acetic acid (1 : 1 : 1)] are significantly larger than the corresponding angles in (**1**).[2,3] The unusual '*anti*' position of the carboxylic O–H bond accompanying the formation of these intramolecular H bonds is worth mentioning, too; from experience, it occurs rarely.[1,6c] Furthermore, the nitrogen atom of the pyridine ring is protonated by the carboxy group to which it is hydrogen bonded, resulting in a positively charged pyridine moiety and a negatively charged carboxy group for the 8,8′-BNDA residue (salt formation). This is, curiously, not indicated by the C–O distances in the respective carboxylate moieties of the binary aggregates, only by those of the ternary complex (see more below).

Table 2. Selected crystal data and experimental details. (E.s.d.s, where given, are in parentheses).

	(**2**)·pyridine (1 : 1)	(**2**)·3-(hydroxymethyl)-pyridine (1 : 1)	(**2**)·pyridine·acetic acid (1 : 1 : 1)
Formula	$C_{22}H_{14}O_4{\cdot}C_5H_5N$	$C_{22}H_{14}O_4{\cdot}C_6H_7NO$	$C_{22}H_{14}O_4{\cdot}C_5H_5N{\cdot}C_2H_4O_2$
M_w	421.4	451.5	481.5
Space group	$P2_1$	*Pbca*	$P\bar{1}$
a/Å	8.080(1)	15.426 7(4)	14.525(6)
b/Å	17.254(2)	21.189 5(6)	10.481(4)
c/Å	7.715(1)	13.372 7(4)	8.862(4)
α/°	90.0	90.0	105.69(4)
β/°	106.28(3)	90.0	111.10(6)
γ/°	90.0	90.0	86.37(6)
Cell volume/Å^3	1 032.4(3)	4 371.3(2)	1 211(1)
Z	2	8	2
D_c/g cm^{-3}	1.36	1.37	1.32
F(000)	440	1 888	504
μ(Cu-K_α)/cm^{-1}	7.02	7.32	7.23
Approximate crystal size/mm	0.48 × 0.57 × 0.48	0.25 × 0.36 × 0.30	0.33 × 0.25 × 0.25
θ_{max}/°	67	67	67
N_{tot} (unique non-zero)	1 909	3 353	3 926
N_{ref} [$F > 6\sigma(F)$]	1 860	2 085	2 686
No. of variables refined	291	311	332
Final agreement factors:			
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.049	0.049	0.053
$R_W = \Sigma w^{\frac{1}{2}}\lvert\Delta F\rvert/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert$	0.045	0.049	0.065
$R_G = [\Sigma w\lvert\Delta F\rvert^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$	0.061	0.048	0.088

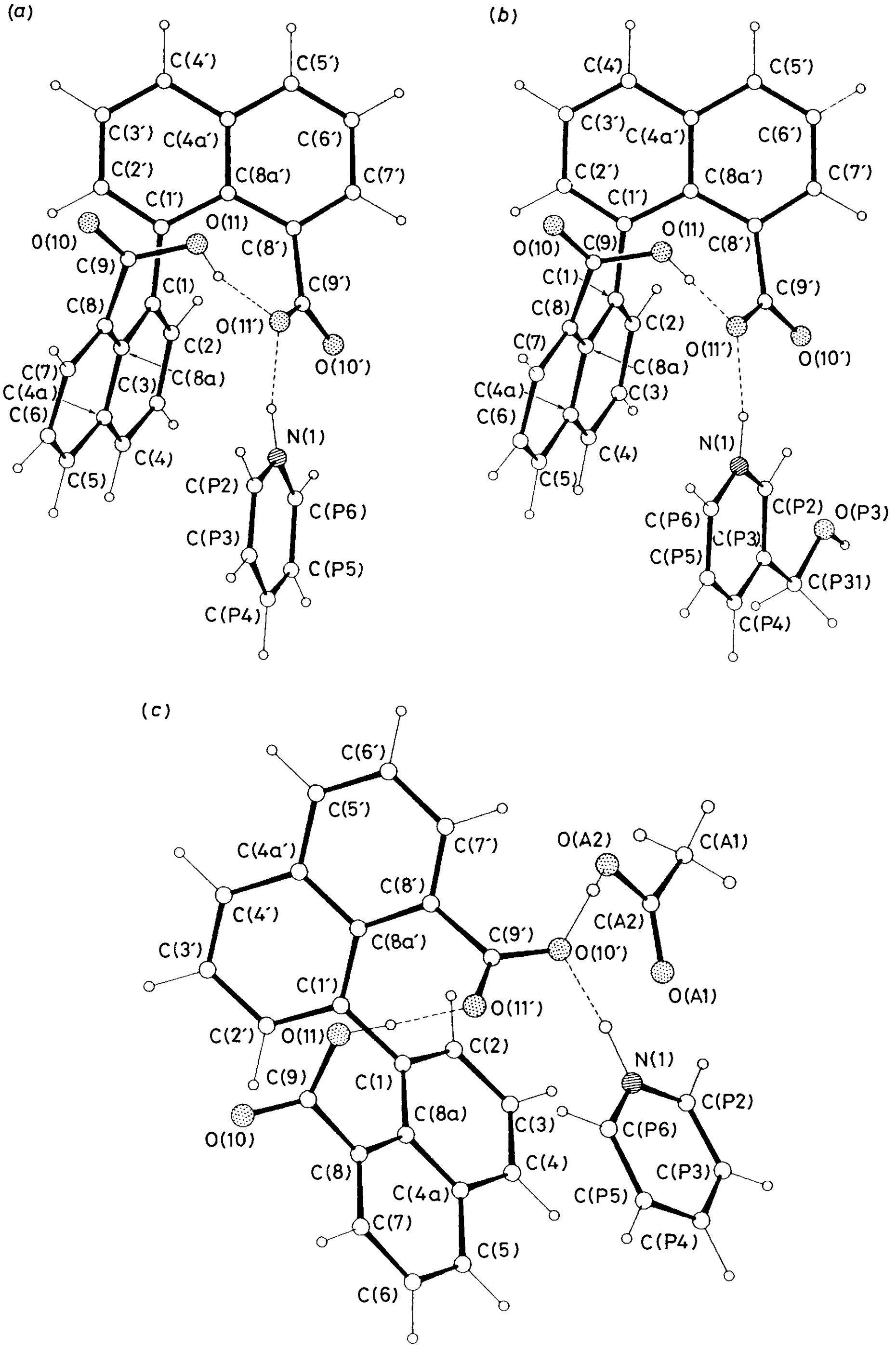


Figure 1. Perspective views of the asymmetric units of the compounds studied: (*a*) (**2**)•pyridine (1:1), (*b*) (**2**)•3-(hydroxymethyl)pyridine (1:1), and (*c*) (**2**)•pyridine•acetic acid (1:1:1). O Atoms are dotted, N atoms, hatched; solid and dashed lines represent covalent and H bonds, respectively.

Packing Features and Host–Guest Interactions.—In the structures of (**2**)•pyridine (1:1) and (**2**)•3-(hydroxymethyl)pyridine (1:1) [Figures 1(*a*) and (*b*)] the carboxylic O(11′) atom is the proton acceptor in an intramolecular and also in an intermolecular H bond (Table 4). In the case of the ternary aggregate (**2**)•pyridine•acetic acid (1:1:1), [Figure 1(*c*)] there is an H bond also from the third component, acetic acid (Table 4). Thus, the O(10′) atom of (**2**) accepts H bonds from both pyridine and acetic acid in this structure, while the O(11′) atom is the proton acceptor in the intramolecular H bond and has a relatively short intermolecular distance [3.138(4) Å] to the pyridine N atom as well. It is probable that this latter contact is a result of combined electrostatic and packing effects. It is notable, however, that the C–O(10′) and C–O(11′) bond distances [1.258(5) and 1.252(5) Å] are equal—within experimental errors—in this structure but not in the other two, which possibly indicates equal engagement for O(10′) and O(11′) in H bond interactions in (**2**)•pyridine•acetic acid (1:1:1). At the same time, the non-equal involvement of the carboxylate oxygens O(10′) and O(11′) in the pyridine and 3-

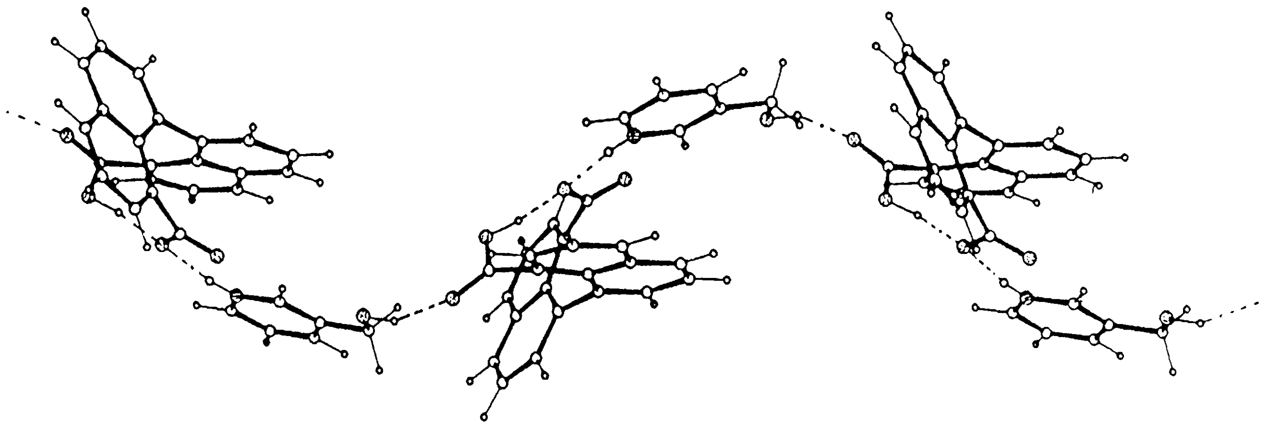


Figure 2. Characteristic fragment of the infinite chains formed by H-bonded heteromolecular aggregates in (2)•3-(hydroxymethyl)pyridine (1:1). O Atoms are dotted, N atoms are hatched. Solid and dashed lines represent covalent and H bonds, respectively.

(hydroxymethyl)pyridine associations with (**2**) [*cf.* Figures 1(*a*) and (*b*)] may be the explanation for the unbalanced C–O distances in these carboxylate anions [C–O(10′) = 1.225(5) and 1.225(5) Å and C–O(11′) = 1.291(4) and 1.296(5) Å in (**2**)•pyridine (1:1) and (**2**)•3-hydroxymethyl)pyridine (1:1), respectively], which approach values of localized single/double bonds fairly well.

Hydrogen bonds between symmetrically related formula units are only observed in (**2**)•3-(hydroxymethyl)pyridine (Figure 2). The hydroxy group of the side chain of the pyridine moiety donates a proton to a carboxy group of a neighbouring 8,8′-BNDA molecule. In this way the heteromolecular aggregates are linked so as to form infinite undulating chains in the crystallographic *c*-direction throughout the structure [Figure 3(*b*)]. In the crystals with pyridine and in the ternary aggregate the structures are built up from finite blocks of H-bonded (**2**)•pyridine and (**2**)•pyridine•acetic acid associations [Figures 3(*a*) and (*c*)]. In these structures the aromatic rings of the pyridine and the binaphthyl moieties are parallel, probably for hydrophobic packing advantages (π–π stacking). Furthermore, it can be seen from the observed intermolecular distances between symmetry related formula units in these latter crystals that there are numerous approaches somewhat shorter than the usual van der Waals' distances. Most of these shorter contacts are between an oxygen atom on the one hand, which is probably slightly negative, and a carbon atom on the other, which is probably slightly positive. It suggests that these crystal structures are held together by an electrostatically favourable molecular packing besides the conventional van der Waals' forces and the possible hydrophobic interactions mentioned above.

In conclusion, the study gives evidence for the truth of a common but unwritten law: bulkiness and crystal inclusion are closely related. The bulky parts of the molecular host framework are important: they are required to construct cavities, but also to prevent the polar groups of any of the individual host molecules from contacting and bonding to one another. In 8,8′-BNDA (**2**), the two functional groups are located so that they can bind to each other and thus work against the net bulkiness of the skeleton. As a consequence—and despite the great similarity to other dicarboxylic hosts known as good co-ordinatoclathrands[1–3,6]—(**2**) has only a modest clathrate-forming ability. Although the present structures are determined by co-operation of biomolecular relevant sites and show interesting modes of H-bonding, structural resemblances to biotic complexes, as in the case of (**1**),[4] are not easy to make out.

Experimental

Synthesis of (RS)-1,1′-*Binaphthyl*-8,8′-*dicarboxylic Acid* (**2**).—Ullmann reaction of 8-bromo-1-naphthoate[10] with copper bronze, according to the literature,[11,12] yielded 48% of (*RS*)-dimethyl-1,1′-binaphthyl-8,8′-dicarboxylate; m.p. 157–159 °C [Cook and Harris[12] obtained two different crystalline forms of this compound from ethanol with m.p. 145–147 °C (plates) and 155–157 °C (elongated prisms), interconvertible by dissolution and appropriate inocculation]. Hydrolysis of the ester with KOH[11,13] and recrystallization from DMSO gave (**2**); yield 87%; m.p. 308–310 °C (decomp.) (lit., m.p. 300–304 °C).[11]

Preparation of the Complexes.—The complexes were obtained by recrystallization of (**2**) from the corresponding pyridine or pyridine-analogous solvent (*cf.* Table 1) or from mixtures of pyridine and the third component used as solvent. On slow cooling, the complexes separated as yellow crystals. Regular parallelepipedic crystals which were grown from dilute solutions were used for the crystallographic studies.

Data Collection and Processing.—The *X*-ray intensity data were collected on a computer-controlled diffractometer at room temperature, using graphite-monochromatized Cu-K_α radiation (λ = 1.5418 Å). The net intensities were corrected for Lorentz and polarization effects but not for absorption. Least-squares fitting of the unit-cell parameters of (**2**)•pyridine (1:1) and (**2**)•pyridine•acetic acid (1:1:1) to a powder pattern, taken in a Guinier–Hägg type focusing camera with strictly monochromatized Cu-K_{α_1} radiation (λ = 1.5406 Å) and Si (a = 5.4309 Å at 298 K) as internal standard, resulted in the values listed in Table 2. The least-squares refinement of the cell parameters of (**2**)•3-(hydroxymethyl)pyridine (1:1) were based on accurately measured angle settings of 53 strong, well centred reflections.

Structure Analysis and Refinement.—Direct methods (MULTAN[14]) were used to calculate the initial phases of the observed reflections. The preliminary structural models were completed and refined using the SHELX[15] program system. The solution of the structure of the ternary complex [(**2**)•pyridine•acetic acid (1:1:1)], was not, however, straightforward. All attempts to complete or refine the initial model obtained from direct methods failed. The solution of the phase problem was found using integrated Patterson and direct methods (PATSEE[16] integrated into the SHELXS[17] system). The Patterson search calculation, using the binaphthyl fragment as search fragment, comprised 70000 rotation and 200 translation trials.

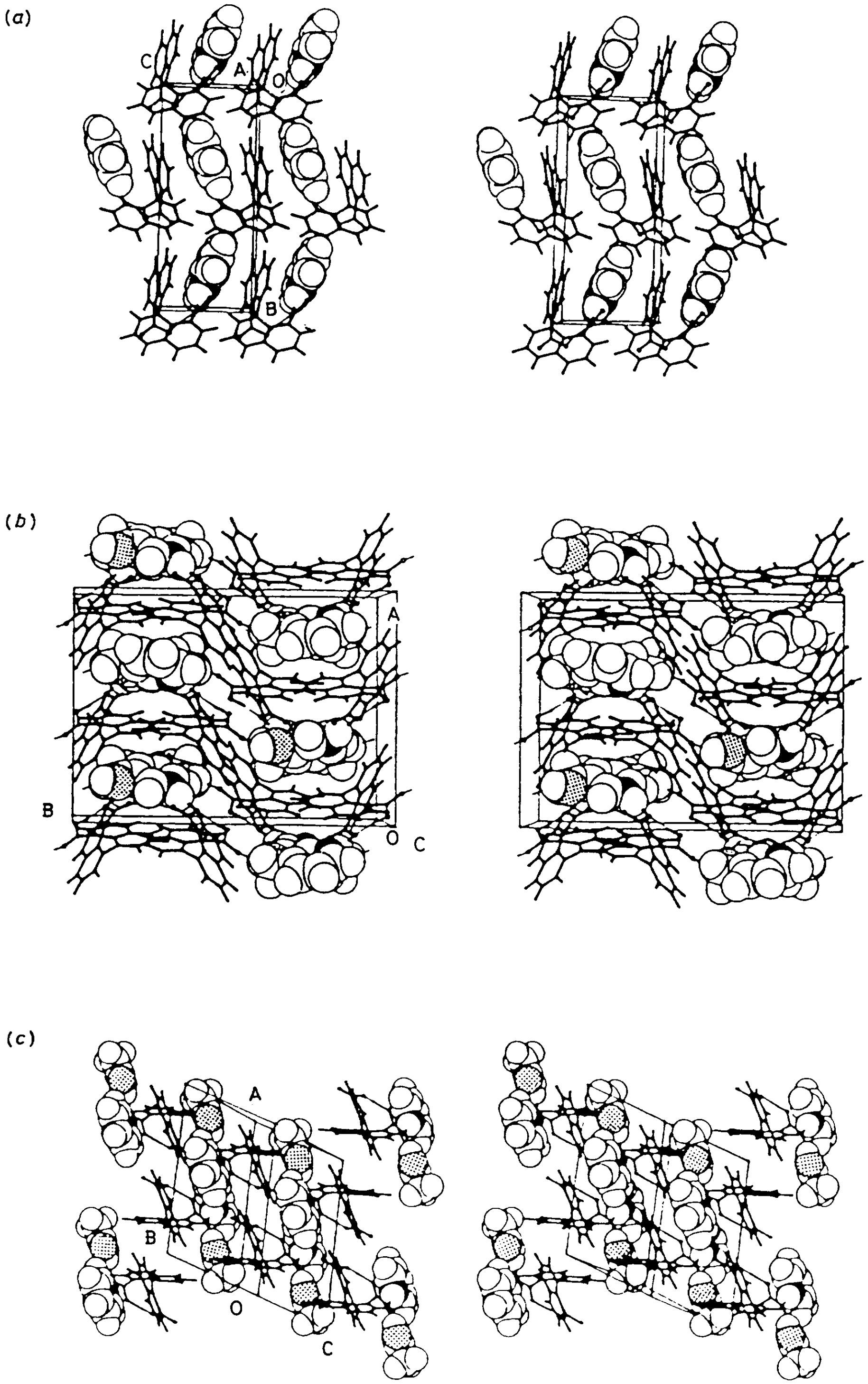


Figure 3. Stereo packing illustrations of: (*a*) (**2**)•pyridine (1 : 1), (*b*) (**2**)•3-(hydroxymethyl)pyridine (1 : 1), and (*c*) (**2**)•pyridine•acetic acid (1 : 1 : 1). The atoms of the pyridine moieties and of acetic acid are drawn with van der Waals' radii; the 8,8′-BNDA molecules are given in stick model fashion. O atoms are dotted, N atoms are filled.

Carbon-bonded H positions were calculated after each cycle of refinements, using geometric evidence. The remaining hydrogens with one exception [in the (**2**)•pyridine•acetic acid (1 : 1 : 1) structure] were located from difference electron density maps and were held fixed in the subsequent calculations. In the final stage of refinement, the positional parameters of the non-H atoms were refined together with their anisotropic temperature parameters. Group isotropic temperature factors were refined for the calculated H positions and individual isotropic temperature factors for the remaining ones. It was noticed, however, that some stronger low-θ reflections had considerably lower F_{obs} than F_{calc}, suggesting extinction effects. These reflections [10 for (**2**)•pyridine (1:1), 7 for (**2**)•3-(hydroxymethyl)pyridine (1:1), and 7 for (**2**)•pyridine•acetic acid (1:1:1)] were excluded from the last calculation when the final R factors (*see* Table 2) were reached. The weights of the structure factors were calculated as $w = k/[\sigma^2(F) + gF^2]$ with the g values refined to 0.000 77 [(**2**)•pyridine (1:1)] and

Table 3. Fractional atomic co-ordinates for the non-hydrogen atoms and for hydrogen atoms involved in the hydrogen bonds. (E.s.d.s, are in parentheses.)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
(**2**)·Pyridine (1:1)			
C(1)	0.148 6(4)	−0.563 7	−0.941 0(4)
C(2)	0.263 1(4)	−0.624 3(4)	−0.882 2(4)
C(3)	0.206 0(5)	−0.700 2(3)	−0.867 3(5)
C(4)	0.034 7(5)	−0.716 1(3)	−0.913 2(5)
C(4a)	−0.087 3(4)	−0.655 8(3)	−0.969 4(4)
C(5)	−0.265 7(4)	−0.673 9(3)	−1.023 5(5)
C(6)	−0.386 5(4)	−0.617 4(3)	−1.080 3(5)
C(7)	−0.335 0(4)	−0.539 9(3)	−1.078 5(4)
C(8)	−0.163 9(4)	−0.519 3(2)	−1.024 8(4)
C(8a)	−0.031 9(4)	−0.577 9(2)	−0.978 0(4)
C(9)	−0.133 0(4)	−0.433 3(3)	−1.014 1(4)
O(10)	−0.203 8(3)	−0.390 7(2)	−1.134 0(4)
O(11)	−0.036 8(3)	−0.404 6(2)	−0.857 0(3)
C(1′)	0.222 3(4)	−0.488 2(2)	−0.977 6(4)
C(2′)	0.182 2(4)	−0.463 2(3)	−1.153 5(4)
C(3′)	0.265 7(4)	−0.400 2(3)	−1.206 2(4)
C(4′)	0.396 5(4)	−0.363 3(3)	−1.082 1(5)
C(4a)	0.441 2(4)	−0.385 8(3)	−0.899 5(4)
C(5′)	0.578 1(4)	−0.348 2(3)	−0.769 8(5)
C(6′)	0.620 7(5)	−0.369 2(3)	−0.593 9(5)
C(7′)	0.525 4(4)	−0.426 1(3)	−0.534 1(5)
C(8′)	0.389 5(4)	−0.463 4(3)	−0.652 6(4)
C(8a′)	0.349 3(3)	−0.447 0(2)	−0.842 0(4)
C(9′)	0.283 0(4)	−0.516 1(3)	−0.570 4(4)
O(10′)	0.351 6(3)	−0.568 6(2)	−0.468 4(4)
O(11′)	0.121 2(3)	−0.499 5(2)	−0.605 9(3)
N(1)	−0.040 7(4)	−0.615 6(3)	−0.506 8(4)
C(2P)	−0.210 2(6)	−0.608 8(3)	−0.534 1(6)
C(3P)	−0.302 5(6)	−0.668 2(4)	−0.493 4(6)
C(4P)	−0.219 0(6)	−0.736 2(3)	−0.423 7(6)
C(5P)	−0.043 7(6)	−0.741 7(4)	−0.394 4(6)
C(6P)	0.041 9(5)	−0.679 7(4)	−0.438 7(5)
H(11)	0.004	−0.444	−0.784
H(1N)	0.017	−0.578	−0.560
(**2**)·3-(Hydroxymethyl)pyridine (1:1)			
C(1)	0.124 5(3)	0.152 4(2)	0.777 6(3)
C(2)	0.126 9(3)	0.213 6(2)	0.743 6(4)
C(3)	0.102 9(3)	0.265 0(2)	0.805 2(4)
C(4)	0.077 2(3)	0.254 0(2)	0.901 9(4)
C(4a)	0.073 8(3)	0.192 3(2)	0.939 5(3)
C(5)	0.047 1(3)	0.181 8(2)	1.040 5(3)
C(6)	0.044 9(3)	0.122 6(2)	1.079 3(3)
C(7)	0.063 4(3)	0.070 8(2)	1.017 8(3)
C(8)	0.085 7(3)	0.078 4(2)	0.918 6(3)
C(8a)	0.094 8(3)	0.140 0(2)	0.877 4(3)
C(9)	0.089 1(3)	0.018 0(2)	0.859 6(3)
O(10)	0.135 1(2)	−0.025 7(2)	0.884 9(2)
O(11)	0.033 0(2)	0.011 7(1)	0.786 1(2)
C(1′)	0.160 4(3)	0.101 8(2)	0.711 5(3)
C(2′)	0.237 8(3)	0.074 9(2)	0.740 0(3)
C(3′)	0.281 8(3)	0.032 0(2)	0.678 2(4)
C(4′)	0.249 5(3)	0.019 2(2)	0.585 4(3)
C(4a′)	0.171 1(3)	0.046 2(2)	0.552 0(3)
C(5′)	0.140 1(4)	0.033 7(2)	0.453 7(3)
C(6′)	0.063 2(4)	0.057 2(2)	0.422 0(4)
C(7′)	0.011 7(4)	0.092 5(2)	0.487 9(3)
C(8′)	0.038 7(3)	0.105 5(2)	0.584 0(3)
C(8a′)	0.121 8(3)	0.085 5(2)	0.617 0(3)
C(9′)	−0.029 2(3)	0.136 2(2)	0.649 2(3)
O(10′)	−0.066 2(2)	0.183 8(2)	0.619 8(3)
O(11′)	−0.048 0(2)	0.108 0(1)	0.732 6(2)
N(1)	−0.136 0(3)	0.194 4(2)	0.843 6(3)
C(2P)	−0.145 0(3)	0.251 3(2)	0.801 3(4)
C(3P)	−0.181 8(3)	0.300 5(2)	0.853 6(4)
C(31P)	−0.192 9(4)	0.364 0(3)	0.805 1(4)
O(3P)	−0.166 5(4)	0.360 9(2)	0.706 5(4)
C(4P)	−0.209 0(3)	0.288 4(3)	0.950 7(4)
C(5P)	−0.199 4(4)	0.229 4(3)	0.992 6(4)
C(6P)	−0.162 6(3)	0.182 3(3)	0.936 6(4)
H(11)	0.006	0.051	0.764
H(1N)	−0.110	0.163	0.800
H(O3P)	−0.175	0.400	0.675
(**2**)·Pyridine·acetic acid (1:1:1)			
C(1)	0.805 7(2)	0.492 9(3)	0.449 0(4)
C(2)	0.866 0(3)	0.569 7(3)	0.418 6(4)
C(3)	0.864 3(3)	0.709 2(4)	0.464 4(5)
C(4)	0.804 0(3)	0.769 4(4)	0.545 4(5)
C(4a)	0.740 6(3)	0.695 0(3)	0.580 8(4)
C(5)	0.679 6(3)	0.761 0(4)	0.670 3(5)
C(6)	0.619 4(3)	0.691 3(4)	0.707 0(5)
C(7)	0.612 2(3)	0.552 1(4)	0.649 6(4)
C(8)	0.667 0(3)	0.484 5(3)	0.556 8(4)
C(8a)	0.737 6(2)	0.554 0(3)	0.527 4(4)
C(9)	0.639 1(3)	0.338 8(3)	0.484 7(4)
O(10)	0.631 4(2)	0.269 2(3)	0.569 0(4)
O(11)	0.613 3(2)	0.289 6(2)	0.320 9(3)
C(1′)	0.822 1(2)	0.347 2(3)	0.411 7(4)
C(2′)	0.861 1(3)	0.290 6(4)	0.544 2(5)
C(3′)	0.891 1(3)	0.158 1(4)	0.517 6(6)
C(4′)	0.885 0(3)	0.086 9(4)	0.362 1(6)
C(4a′)	0.844 8(3)	0.139 7(3)	0.222 3(5)
C(5′)	0.840 3(3)	0.065 3(4)	0.060 0(6)
C(6′)	0.800 8(3)	0.116 7(4)	−0.074 0(5)
C(7′)	0.759 3(3)	0.241 9(4)	−0.055 5(5)
C(8′)	0.759 6(2)	0.316 0(3)	0.098 8(4)
C(8a′)	0.807 8(2)	0.270 5(3)	0.244 9(4)
C(9′)	0.695 8(3)	0.434 8(3)	0.096 6(4)
O(10′)	0.708 7(2)	0.519 3(2)	0.028 1(3)
O(11′)	0.627 4(2)	0.441 2(2)	0.152 7(3)
N(1)	0.621 0(3)	0.738 8(4)	0.143 0(4)
C(2P)	0.660 8(4)	0.851 5(4)	0.156 8(7)
C(3P)	0.627 4(4)	0.966 9(5)	0.223 7(7)
C(4P)	0.551 3(4)	0.966 9(4)	0.281 3(6)
C(5P)	0.509 4(4)	0.849 3(5)	0.268 4(6)
C(6P)	0.547 8(4)	0.732 3(4)	0.197 3(5)
C(1A)	0.973 3(4)	0.682 7(5)	−0.073 6(7)
C(2A)	0.896 0(3)	0.664 2(4)	−0.008 5(5)
O(1A)	0.869 3(3)	0.751 1(3)	0.086 8(5)
O(2A)	0.857 0(2)	0.543 0(3)	−0.066 1(4)
H(11)	0.618	0.349	0.259
H(1N)	0.648	0.648	0.085
H(2A)	0.809	0.534	−0.040

0.012 77 [(**2**)·pyridine·acetic acid (1:1:1)]. In the refinement of the (**2**)·3-(hydroxymethyl)pyridine (1:1) structure, all the reflections had unit weight.

In the structures of the two-component aggregates, (**2**)·pyridine (1:1) and (**2**)·3-(hydroxymethyl)pyridine (1:1), difference electron density calculations revealed the H atom between the O(11′) and the N(1) atoms [*cf.* Figures 1(*a*) and (*b*)] to be covalently bound to the nitrogen atom. In order to add weight to the evidence for the pyridinium moieties, the final refinement calculations of these structures were repeated including also the refinement of the position of this particular H(N1) atom. The results of these latter calculations were practically identical with the earlier ones [*i.e.* with fixed H(N1) position] except for minor translations of the H(N1) atoms: in the case of (**2**)·pyridine (1:1) the H(N1)–N(1) distance changed from 0.963 to 0.894(61) Å, while for the (**2**)·3-(hydroxymethyl)-pyridine (1:1) the same bond length increased from 0.973 to 1.007(50)Å. These changes are, however, in the range of the e.s.d.s of the refined positions.

In the structure of (**2**)·pyridine·acetic acid (1:1:1), the difference Fourier calculations did not result in any peak in the vicinity of the pyridine N atom, where the missing H atom is

Table 4. Distances/Å and angles/° in possible hydrogen bonding contacts. (E.s.d.s, where given, are in parentheses.)

Atoms involved	Donor···Acceptor	Donor–H	H···Acceptor	Donor–H···Acceptor angle
(**2**)·pyridine (1:1)				
O(11)–H(11)···O(11′)	2.585(4)	0.88	1.73	163
N(1P)–H(1N)···O(11′)	2.620(5)	0.96	1.68	166
(**2**)·3-(hydroxymethyl)pyridine (1:1)				
O(11)–H(11)···O(11′)	2.497(3)	0.99	1.52	172
N(1)–H(1N)···O(11′)	2.720(4)	0.97	1.76	171
O(3P)–H(30P)···O(10)[a]	2.740(5)	0.95	1.86	153
(**2**)·pyridine·acetic acid (1:1:1)				
O(11)–H(11)···O(11′)	2.516(4)	0.96	1.56	178
N(1P)–H(1N)···O(10′)	2.693(4)	1.08	1.62	169
O(2A)–H(2A)···O(10′)	2.622(5)	0.82	1.80	177

[a] Symmetry operation: $-x, \frac{1}{2} + y, \frac{1}{2} - z + 1$.

assumed to be. This nitrogen atom is situated near to two potential proton acceptor atoms [N···O(10′) = 2.693(4) and N···O(11′) = 3.138(4) Å, angle O(10′)···N···O (11′)- = 43.5(1)°]. This may be the reason why the position of the (N)–H atom could not be found from *X*-ray data. The last refinement of the (**2**)·pyridine·acetic acid (1:1:1) structure was performed twice: first without the (N)–H atom and then including the calculated (N)–H position. These refinements converged to the reliability indices $R = 0.0543$ and 0.0527 and $R_w = 0.0666$ and 0.0652 for the first and second refinement, respectively. The results presented in this paper are based on the second calculation.

Compound (**2**)·pyridine (1:1) crystallizes in optically pure form. Determination of the absolute configuration based on the *X*-ray data was, however, not feasible, because the crystal contains only 'light' atoms which yield only slightly anomalous dispersion effects.[18] The last refinement of the two enantiomers resulted in slightly different *R* values: 0.0493/0.0490 and 0.0457/0.0453 for the linear *R* and for the weighted *R*,[15] respectively. The enantiomer giving the 'lower' *R* values is presented here.

Supplementary Data.—Lists of bond lengths and bond angles involving the non-H atoms, contact distances < 3.45 Å between symmetry related formula units, fractional atomic co-ordinates of the calculated H positions, and thermal parameters have been deposited as supplementary data at the Cambridge Crystallographic Data Centre.*

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* *Supplementary data:* for details of the supplementary publications scheme see 'Instructions for Authors' (1989), *J. Chem. Soc., Perkin Trans. 2*, in the January issue.