Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 101, No. 4, August 1989, pp. 327–334.

Clathrate compound of a new host material, 3-hydroxy-6-(4′-nitro)phenylazopyridine

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MS received 2 May 1988

Abstract. The compound 3-hydroxy-6-(4′-nitro)phenylazopyridine (1) was observed to incorporate several organic solvents of crystallisation, forming stable clathrates. These clathrates decompose upon heating and the host material is chemically transformed. Single crystal X-ray diffraction studies on the ethanol clathrate lead to a reasonable model for the host structure. But the guest molecules are severely disordered. Alternatively, the compound forms twinned crystals. The chemically closely related compound 2 does not form clathrates.

Keywords. Clathrates; azo dye; crystallography; disorder; twinning; solid state reaction.

1. Introduction

Host–guest compounds are two component systems where one component, the guest species, is accommodated in the voids formed in the crystal structure of the second component, the host (Davies 1981; Weber 1987). Such compounds may be further subdivided as: (i) clathrates, in which the guest species are completely enclosed within the cavity formed by the host molecules, (ii) intercalates, in which the guest is accommodated in the interlayer spaces of the host, and (iii) inclusion compounds in which the guest is accommodated in channels formed by the host.

The general tendency of molecular crystals is to close-pack (Kitaigorodskii 1973). This is true not only for hydrocarbons where van der Waals interactions are important but also for heteroatom derivatives, where various kinds of directional interactions (hydrogen bonding, dipole–dipole) must be considered. However, due to a combination of factors, some molecules are unable to close-pack in the usual sense. When conflicting or irreconcilable demands are placed on the packing by factors such as the molecular symmetry and the preferred directionality of non-bonded contacts, molecules tend to crystallise in relatively 'open' arrangements which may take up solvent or other molecules as guest species. Typical examples are the triphenylmethanes (Driver *et al* 1955, 1958), perhydrotriphenylene (Colombo and Allegra 1971; Farina 1984), hydroquinone (Powell 1948) and trimesic acid (Duchamp and Marsh 1969).

Till recently, the commonly held view was that new host materials could only be

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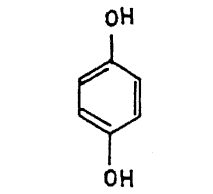
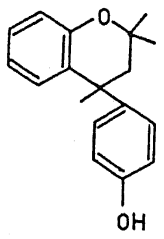
found by chance, since most organic molecules pack efficiently leaving no significant voids which may accommodate the guest molecules. In fact, there is no general principle to predict just what molecular features promote the tendency to adopt a host-type crystal structure. Therefore it seems reasonable to ask whether it is possible to synthesize new compounds which though unrelated to any known host lattice would be expected to have host lattices.

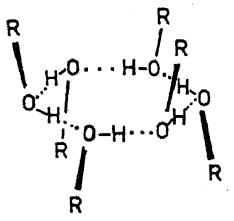
Host molecules such as hydroquinone, phenol and Dianin's compound (Powell 1948; Flippen *et al* 1970) whose early discoveries were accidental have a symmetrical network of hydrogen bonds formed by the linking of $-OH$ groups of six host molecules such that the oxygen atoms form a hexagonal arrangement. MacNicol and coworkers have compared this arrangement with hexasubstituted benzenes and by choosing suitable substituents it is possible that hexasubstituted benzenes also act as host lattices (MacNicol *et al* 1978; MacNicol 1984). Another strategy employed by Toda and Akagi (1968) and Hart *et al* (1984) is the design of host molecules which look like a wheel and axle. These molecules are characterised by a long molecular axis of *sp* carbons with sp^3 carbons at each end bearing relatively bulky groups. The larger



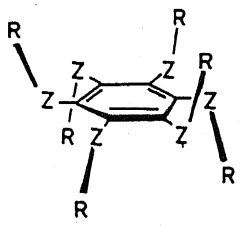
Hydroquinone



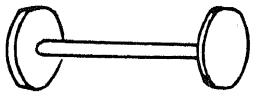
Dianin's compound



Hydrogen-bonded hexamer unit



Hexa host



Wheel and axle

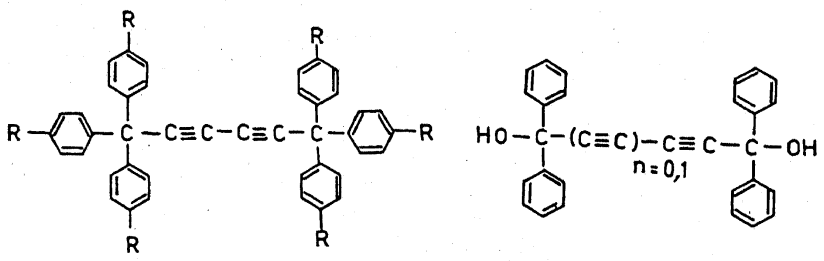


Chart I

terminal groups act as spacers which prevent the host molecule from adopting a close-packed arrangement in the crystal, consequently forming large voids.

The present study was initiated because it was found that the title compound forms several solvated crystals from common organic solvents.

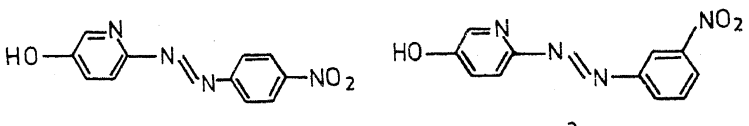
2. Experimental

The compound 3-hydroxy-6-(4′-nitro)phenylazopyridine (1) was prepared according to the literature procedure (Moore and Marascia 1959). The material was recrystallised from solvents such as ethanol, methanol, acetone, ethyl acetate and *iso*-propanol. Heating experiments were performed in an oil bath.

3. Results and discussion

3-Hydroxy-6-(4′-nitro)phenylazopyridine (1) has been reported as existing in three polymorphic modifications, namely orange, red and violet needles (Moore and Marascia 1959). But upon recrystallisation from different solvents (like ethanol, methanol, ethyl acetate, acetone and *iso*-propanol) it was found that the compound is not polymorphic at all but rather forms clathrates. An indication of clathrate formation is that the densities of the crystals obtained from various solvents are slightly but significantly different. Since the crystals obtained from ethanol could be studied by the X-ray method the calculated density may also be estimated. This value is 1·20 g/cm^3, assuming no solvent in the crystal. This is strikingly different from the experimentally found density for the ethanol clathrate which is 1·43 g/cm^3. This latter value is in good agreement with the density calculated for one molecule of ethanol per each molecule of the host (1·40 g/cm^3). Experimental densities of methanol, acetone, *iso*-propanol, and ethyl acetate clathrates were found to be 1·44 $\pm$ 0·005 g/cm^3 and are in the same range as the ethanol clathrate. If the assumption is made that the cell parameters of the other clathrates are similar to those of the ethanol clathrate, it may be concluded from the observed densities that the above solvents are also included in the host lattice. Our confidence in these numbers is strengthened by the fact that in the related non-clathrate forming 3-hydroxy-6-(3′-nitro)phenylazopyridine, (2), the experimental and calculated densities were found to be very nearly the same (1·46 and 1·47 g/cm^3) (Desiraju and Krishna 1988).

The different clathrates were heated at 150°C for about two hours in an oil bath. All the compounds turned into a dark green substance which is practically insoluble in common organic solvents (λ_{max}, 510–514 nm). Solutions of this latter compound in dimethyl sulphoxide are pale pink in colour. The low resolution mass spectrum of the green residue showed a peak at 848(*m/e*). The IR and UV spectra of the green



1 2

Chart II

compound were found to be independent of the solvent of clathration. The fact that the same green compound is formed from all the clathrates shows that the material is undergoing some solid state reaction which may be characteristic of the host lattice itself.

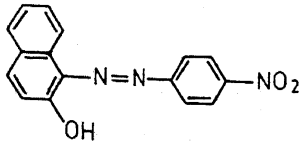
3.1 *Crystal structure determination of the ethanol clathrate*

In contrast with the non-clathrate-forming 2, the crystal structure of which has already been determined (Desiraju and Krishna 1988), the crystal structure determination of 1 was very problematic. These difficulties have not been fully resolved in the present study.

The crystal structure of 1 was determined from data collected in two distinct space groups $P2_1/n$ and $P\bar{1}$. In both cases, the cell parameters are very nearly the same. When data were collected in the space group $P2_1/n$, the α and γ angles were found to be slightly different from 90°. Further, some high angle reflections have significantly different intensities for hkl and $\bar{h}\bar{k}\bar{l}$. It appears therefore that the triclinic space group $P\bar{1}$ is the correct space group for clathrate 1 and all further discussion deals with data collected in this space group.

Space group	a	b	c	α	β	γ
$P2_1/n$	7·110	18·321	11·092	90·00	107·92	90·00
$P\bar{1}$	7·026	18·344	10·973	89·99	107·42	90·06

Single crystal data were collected on an Enraf-Nonius CAD-4 diffractometer at the Max Planck Institut fur Polymerforschung, Mainz. The structure was solved using the SHELXS86 program (Sheldrick 1986, $F(000) = 608$, $Z = 4$, $\lambda(\mathrm{MoK}_\alpha) = 0{\cdot}7107$ Å) on 1372 reflections at the 2σ level and refined using the SHELX76 program (Sheldrick 1976). The refinement was stopped at the isotropic stage with the R-factor being 0·195. The atom labelling scheme is given in figure 1. The atomic coordinates, bond lengths and angles are given in tables 1–4. The shortest intermolecular contact is 2·81 and 2·82 Å between the N(3) of one symmetry independent molecule and the O(3) of another symmetry-independent molecule. The R-factor of 0·195 is relatively high and means that there is much unaccounted electron density. A careful search of the Fourier difference map revealed the presence of the solvent molecule ethanol. But the solvent failed to refine properly. As seen from the stereo plot (figure 2), the ethanol molecules are very close to inversion centres at 0 1/2 0 and 0 0 1/2. This will bring the two symmetrically related ethanol molecules unacceptably close. This implies that the ethanol is disordered between these two positions with partial occupancies in the two



Para red

Chart III

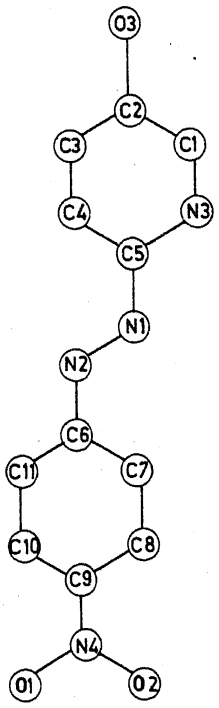


Figure 1. Atom labelling scheme for compound 1

Table 1. Atomic coordinates in fractional crystal coordinates for the compound 1 in $P\bar{1}$ space group (e.s.d's are given in parentheses).

	Molecule A		
Atom	*x/a*	*y/b*	*z/c*
C(1)	−0·013(4)	0·241(1)	0·394(2)
C(2)	−0·095(3)	0·241(1)	0·262(2)
C(3)	−0·099(3)	0·303(1)	0·189(2)
C(4)	0·000(4)	0·365(1)	0·256(2)
C(5)	0·086(4)	0·360(1)	0·393(2)
C(6)	0·271(4)	0·535(2)	0·496(3)
C(7)	0·364(4)	0·526(1)	0·631(3)
C(8)	0·451(3)	0·586(1)	0·703(2)
C(9)	0·452(3)	0·653(1)	0·637(2)
C(10)	0·378(4)	0·664(1)	0·514(2)
C(11)	0·281(3)	0·603(1)	0·439(2)
N(1)	0·180(3)	0·420(1)	0·470(2)
N(2)	0·176(3)	0·478(1)	0·412(2)
N(3)	0·082(3)	0·301(1)	0·455(2)
N(4)	0·548(3)	0·718(1)	0·719(2)
O(1)	0·567(3)	0·772(1)	0·664(2)
O(2)	0·602(3)	0·707(1)	0·835(2)
O(3)	−0·193(2)	0·178(1)	0·212(2)
S(1)	−0·265(8)	1·004(3)	−0·501(4)
S(5)	−0·086(7)	0·974(2)	−0·486(4)
S(6)	−0·388(7)	0·947(3)	−0·435(5)

S(1), S(5), S(6) refer to solvent atoms.

Table 2. Atomic coordinates in fractional crystal coordinates for the compound 1 in $P\bar{1}$ space group (e.s.d's are given in parentheses).

	Molecule B		
Atom	*x/a*	*y/b*	*z/c*
C(1)	0·511(4)	0·741(1)	0·105(2)
C(2)	0·593(3)	0·741(1)	0·237(2)
C(3)	0·597(3)	0·803(1)	0·311(2)
C(4)	0·500(4)	0·866(1)	0·244(2)
C(5)	0·413(3)	0·860(1)	0·109(2)
C(6)	0·224(4)	1·035(1)	0·001(2)
C(7)	0·137(4)	1·024(1)	−0·133(2)
C(8)	0·050(3)	1·087(1)	−0·202(2)
C(9)	0·045(4)	1·151(1)	−0·139(3)
C(10)	0·123(4)	1·164(1)	−0·013(2)
C(11)	0·220(4)	1·100(1)	0·062(2)
N(1)	0·320(3)	0·919(1)	0·030(2)
N(2)	0·324(3)	0·977(1)	0·088(2)
N(3)	0·418(3)	0·802(1)	0·045(2)
N(4)	−0·050(3)	1·219(1)	−0·221(2)
O(1)	−0·066(3)	1·273(1)	−0·164(2)
O(2)	−0·103(3)	1·206(1)	−0·336(2)
O(3)	0·695(3)	0·678(1)	0·287(2)
S(2)	−0·236(8)	0·505(3)	−0·002(5)
S(7)	−0·125(7)	0·445(3)	−0·070(5)
S(8)	−0·414(7)	0·475(3)	−0·013(5)

S(2), S(7), S(8) refer to solvent atoms.

Table 3. Bond lengths in Å and angles in degrees for the compound 1 (molecule A) in space group $P\bar{1}$.

Bond lengths			
C(1)–C(2)	1·39(3)	C(1)–N(3)	1·36(3)
C(2)–C(3)	1·39(3)	C(5)–N(3)	1·28(3)
C(3)–C(4)	1·42(3)	C(5)–N(1)	1·42(3)
C(4)–C(5)	1·45(3)	C(6)–N(2)	1·42(4)
C(6)–C(7)	1·44(5)	C(9)–N(4)	1·52(3)
C(7)–C(8)	1·39(3)	N(1)–N(2)	1·24(3)
C(8)–C(9)	1·43(3)	N(4)–O(1)	1·19(3)
C(9)–C(10)	1·31(3)	N(4)–O(2)	1·23(3)
C(10)–C(11)	1·43(3)	S(1)–S(6)	1·65(7)
C(11)–C(6)	1·41(4)	S(1)–S(5)	1·34(7)
C(2)–O(3)	1·37(3)		
Bond angles			
C(2)–C(1)–N(3)	120(1)	N(2)–C(6)–C(11)	116(3)
C(1)–C(2)–O(3)	115(2)	C(7)–C(6)–C(11)	119(1)
C(3)–C(2)–O(3)	123(2)	C(6)–C(7)–C(8)	119(2)
C(1)–C(2)–C(3)	122(2)	C(7)–C(8)–C(9)	118(2)
C(2)–C(3)–C(4)	116(2)	C(8)–C(9)–C(10)	127(1)
C(3)–C(4)–C(5)	118(1)	C(8)–C(9)–N(4)	116(2)
C(4)–C(5)–N(3)	122(2)	C(10)–C(9)–N(4)	117(2)
N(1)–C(5)–N(3)	115(2)	C(9)–C(10)–C(11)	116(2)
N(1)–C(5)–C(4)	123(2)	C(10)–C(11)–C(6)	121(2)
C(5)–N(3)–C(1)	121(2)	C(9)–N(4)–O(1)	117(2)
C(5)–N(1)–N(2)	115(2)	C(9)–N(4)–O(2)	115(2)
N(1)–N(2)–C(6)	111(2)	O(1)–N(4)–O(2)	128(2)
N(2)–C(6)–C(7)	124(2)	S(5)–S(1)–S(6)	106(3)

Table 4. Bond lengths in Å and angles in degrees for the compound 1 (molecule B) in space group $P\bar{1}$.

Bond lengths			
C(1)–C(2)	1·39(3)	C(1)–N(3)	1·36(3)
C(2)–C(3)	1·39(3)	C(5)–N(3)	1·28(3)
C(3)–C(4)	1·43(3)	C(5)–N(1)	1·42(3)
C(4)–C(5)	1·43(3)	C(6)–N(2)	1·46(3)
C(6)–C(7)	1·43(3)	C(9)–N(4)	1·57(3)
C(7)–C(8)	1·42(3)	N(1)–N(2)	1·24(3)
C(8)–C(9)	1·37(3)	N(4)–O(1)	1·19(3)
C(9)–C(10)	1·35(4)	N(4)–O(2)	1·23(3)
C(10)–C(11)	1·48(3)	S(2)–S(7)	1·65(8)
C(11)–C(6)	1·37(3)	S(2)–S(8)	1·34(8)
C(2)–O(3)	1·38(3)		
Bond angles			
C(2)–C(1)–N(3)	120(1)	N(2)–C(6)–C(11)	113(1)
C(1)–C(2)–O(3)	115(2)	C(7)–C(6)–C(11)	124(2)
C(3)–C(2)–O(3)	122(2)	C(6)–C(7)–C(8)	115(2)
C(1)–C(2)–C(3)	123(2)	C(7)–C(8)–C(9)	120(2)
C(2)–C(3)–C(4)	116(2)	C(8)–C(9)–C(10)	127(2)
C(3)–C(4)–C(5)	118(2)	C(8)–C(9)–N(4)	118(2)
C(4)–C(5)–N(3)	124(2)	C(10)–C(9)–N(4)	115(2)
N(1)–C(5)–N(3)	112(1)	C(9)–C(10)–C(11)	114(2)
N(1)–C(5)–C(4)	123(2)	C(10)–C(11)–C(6)	119(1)
C(5)–N(3)–C(1)	120(2)	C(9)–N(4)–O(1)	117(2)
C(5)–N(1)–N(2)	114(1)	C(9)–N(4)–O(2)	112(1)
N(1)–N(2)–C(6)	111(2)	O(1)–N(4)–O(2)	131(2)
N(2)–C(6)–C(7)	123(2)	S(7)–S(2)–S(8)	104(5)

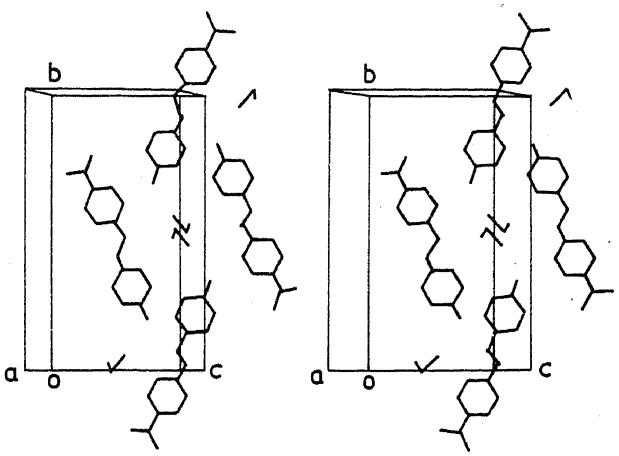


Figure 2. A stereoview of the crystal packing of the ethanol clathrate of compound 1. Notice the guest molecules in channels which run down [100].

sites. But refinement incorporating such partial occupancies was not successful.

Another reason for the high *R*-factor is the possibility of twinning of the crystal which may not be detected easily. This possibility was considered since the related compound para red shows a subtle kind of twinning which was only resolved with difficulty (Grainger and McConnell 1969).

From figure 2 the channels to accommodate the guest molecules can be seen very clearly. The N(3)... O(3) hydrogen bonding is parallel to the *bc* plane whereas the channels are located along the *a* direction. This makes the escape of the solvent upon heating in the *b* and *c* directions difficult as it has to cross the zigzag path in that direction. Escape of the solvent along the *a* direction seems to be easier.

Since prolonged heating is necessary to drive the solvent out of the crystal lattice, it can be concluded that the solvent is firmly bound within the crystal lattice. This type of attachment is difficult without some sort of hydogen bonding. However, this might seem to suggest an ordered guest structure not observed in the present case. The host structure collapses, in fact transforms chemically, if an attempt is made to drive the solvent from the crystal by heating. The observed host lattice is clearly stabilized by the presence of the guest.

3.2 *X-Ray powder diffraction studies*

X-ray powder patterns were recorded for the methanol clathrate dried under different conditions like ordinary drying (56°C), vacuum drying (1 torr) and vacuum drying with heating (56°C, 1 torr). The θ values for the powder pattern decrease systematically in the order: ordinary drying, vacuum drying and vacuum drying with heating (table 5) indicating increasing values of d, which suggests that the crystal lattice is expanding as one proceeds from vacuum drying to vacuum drying with heating. Upon heating, it may be expected that the solvent molecules occupy more space in the lattice due to increasing thermal motion and in order to accommodate the guest, the host lattice perhaps expands. Further, the powder pattern of methanol clathrate dried at different conditions are roughly the same but show a small increase in d value which means that the guest is not eliminated very easily during the drying process but that heating may expand the crystal lattice slightly.

Table 5. X-ray powder pattern (*d* values, CuK_α) of methanol clathrate of dye 1 under different drying conditions.

Air drying	Vacuum drying	Vacuum drying with heating
8·63	8·84	9·03
6·63	6·76	6·94
5·11	5·19	5·34
4·87	4·93	5·07
4·40	4·46	4·59
3·24	3·28	3·33

The clathrates of dye 1 obtained from other solvents (ethanol, methanol, acetone, ethyl acetate and *iso*-propanol) show different powder patterns which may indicate the presence of solvent in the crystal lattice. In contrast, the *meta*-nitro dye 2 shows identical powder diffraction patterns for materials crystallised from different solvents indicating that the crystalline form obtained is independent of the solvent used.

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