JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. **12**, 157–164 (1999)

Disorder as adaptation of the crystal structure to increase the crystallization temperature. X-ray crystal structure of the host–guest complexes between 1,1′-binaphthyl-2,2′-dicarboxylic acid and dimethyl sulphoxide obtained at 50 and 60 °C

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Received 1 Feburary 1998; revised 27 May 1998; accepted 28 May 1998

ABSTRACT: The complex formation of 1,1′-binaphthyl-2,2′-dicarboxylic acid (BNDA) with dimethyl sulphoxide (DMSO) at different temperatures was investigated. The crystal structures of the α- and β-form [triclinic, $P\bar{1}$, $a = 9.614(2)$, $b = 11.743(2)$, $c = 12.029(2)$ Å, $\alpha = 99.35(3)$, $\beta = 93.58(3)$, $\gamma = 110.51(3)°$, $V = 1244.5(4)$ Å^3, $Z = 2$, $R = 0.053$ for 4879 reflections] host–guest complexes obtained at 50 and 60 °C, respectively, were determined by x-ray structure analysis (the crystal structure of the α-form obtained at room temperature was studied previously). There is disorder of the guest molecules characteristic of the α-form of the 1:1 BNDA·DMSO complex obtained at 50 °C and the host carboxylic groups in the β-form of the 1:2 BNDA·DMSO, considered a consequence of the changed conditions for crystal preparation. By disordering of the crystal structure the interaction of the solvent molecule with its environment, especially with nearest BNDA molecules, is improved. The new orientation leads to the formation of a more compact host–guest associate which resists the escape of the guest molecules from the growing crystal during crystallization and may exist even in the nucleation step. Thus disordering of the solvent molecules (α-form) and disordering of the carboxyl groups of the host molecules (β-form) are the two modes of operation in this system.

KEYWORDS: crystalline complexes; dicarboxylic acid host; dimethyl sulphoxide guest; x-ray crystal structure; pseudopolymorphism; hydrogen bonding

INTRODUCTION

Crystalline host–guest compounds are objects of considerable attention owing their promising behaviour.[1] They make possible a wide range of applications, especially the separation and retrieval of chemical species differing in chemical nature, dimensions and shape of molecules or chirality. Odorous, toxic and hazardous substances may be solidified *via* inclusion, reducing their vapour pressure and volatility, allowing controlled, retarded and suppressed release.[2] Recently a new field of application of the host–guest compounds to chemical sensor development has been discovered.[3] All this has stimulated a great demand for easily obtainable compounds serving as typical hosts in the crystalline state.

In order to design new host structures, different approaches have been applied in recent years, such as the 'hexa-host' strategy,[4] the 'wheel-and-axle' simile and the concept of symmetry-constrained host molecules.[5] Moreover, one may refer to the coordinatoclathrate concept for predicting the main principles of the solid-state host–guest association.[6]

However, there is another unique way to prepare new host–guest complexes apart from the synthesis of new host compounds. Having a crystalline inclusion complex with a definite host and a given guest, one can try to obtain a new modification of the clathrate for this host–guest pair. This may be achieved by controlling the crystallization conditions, *i.e.* changing the concentration, temperature and pressure in the crystallization medium. This approach has proved efficient in the example of several well known versatile hosts such as gossypol[7] and its derivatives,[8,9] cyclotriveratrylene[10] and

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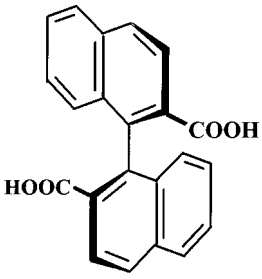
Contract/grant sponsor: Deutsche Forschungsgemeinschaft.
Contract/grant sponsor: Fonds der Chemischen Industrie.

 CCC 0894–3230/99/020157–08 $17.50



Scheme 1. BNDA

others.[11,12] Applying the same principle to the complex formed between 1,1′-binaphthy1-2,2′-dicarboxylic acid (BNDA) (Scheme 1) and ethanol, exhibiting both proton donor and acceptor abilities, we succeeded in preparing a new modification of the clathrate including half the content of the guest component and also the guest free host.[13]

Previously, a 1:1 coordinatoclathrate of BNDA with dimethyl sulphoxide (DMSO) was obtained and its x-ray crystal structure determined.[14] In order to apply the above-mentioned strategy to the complex with the aprotic solvent DMSO, showing only proton acceptor properties, in this work we investigated host–guest formation between BNDA and DMSO at different temperatures. At 50 °C the known 1:1 clathrate (α-form) was obtained but crystallization at 60 °C gave rise to a new (β-form) modification with a 1:2 host:guest stoichiometric ratio. In the hope of obtaining rearrangements caused by the influence of temperature, we decided to determine the respective crystal structures. This paper is devoted to a discussion of the crystal structures of the α- and β-forms of BNDA·DMSO complexes.

RESULTS AND DISCUSSION

Molecular structures

The general features of the host conformation are a dihedral angle between the naphthyl moieties, coplanarity of the atoms of these moieties and an orientation and inclination of the carboxyl groups to the naphthyl fragments. The former features of the BNDA conformation are similar in all previously studied crystals,[6] *i.e.* the planes of the naphthyl fragments are nearly perpendicular to each other and atoms of these fragments are coplanar to a great extent. In the α- and β-form complexes, the naphthyl moieties are tilted at an angle of 80.5(2)° and 88.6(2)° to each other, respectively (Fig. 1). The carboxyl groups may be differently inclined relative to the respective naphthyl fragment in the different complexes. The observed dihedral angles are 8.0(4)° and 30.2(2)° for the α-form. In the β-form complex, one group is located in two and the other in three different positions [Fig. 2(a)]. These two- and threefold disordered groups are different in site occupation factors (sof) and therefore each of them may be characterized as major and minor orientations. In the major orientation the —CO(2)O(1)H group with sof = 0.87(1) is more tilted [21.8(4)°] than in minor orientation with sof 0.13(1) inclined to 7(1)°. The carboxyl group of the other half has three different orientations with sof = 0.73(1), 0.13(1) and 0.14(1). Dihedral angles of the —CO(2)O(1)H group to the parent naphthyl nuclei in major and minor (**A** and **B**) orientations are 10.8(4)°, 40(1)° and 45.9(8)°, respectively.

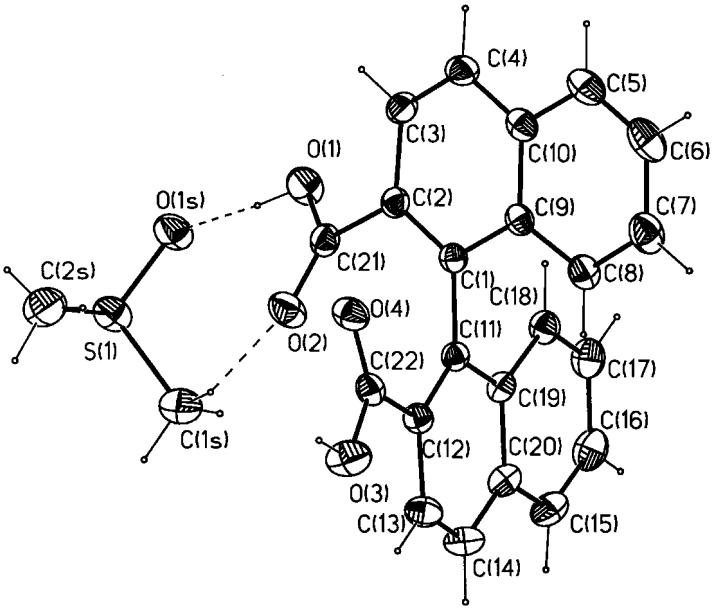
It should be noted that the intrinsic symmetry C_2 of the host molecule is lost in both the previous BNDA·DMF[14] and the β-form BNDA·DMSO complex. In these conformations two carboxyl groups of BNDA are differently oriented to the respective naphthyl fragment in order to form a relatively strong intermolecular H-bond between the carboxyl hydroxy group and the oxygen atom of the solvent molecule [Fig. 1(b)].

The bond distances and angles of the BNDA molecules are in good agreement with those found in early studied structures.[13–15]

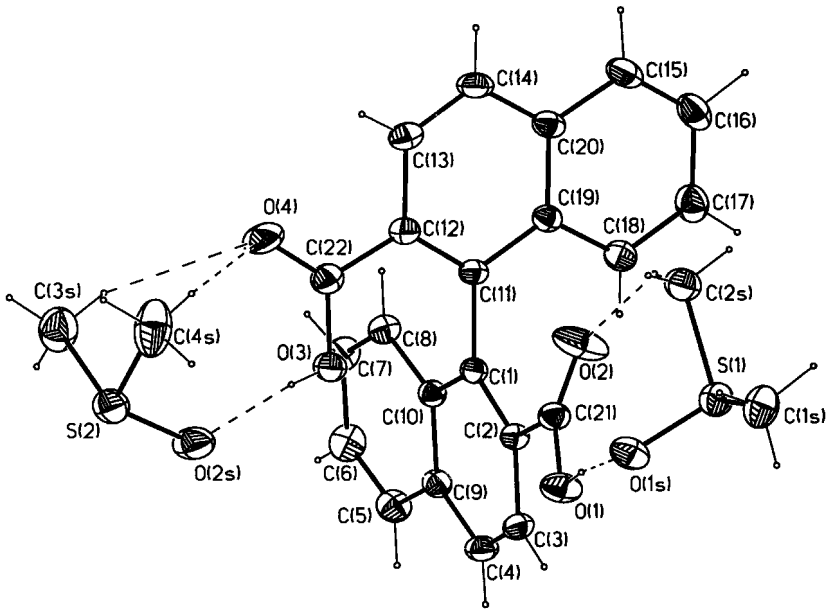
Crystal structure of the α-form

In the crystal of the 1:1 BNDA·DMSO complex,[14] solvent molecules show double-acceptor abilities, incorporating host molecules in the infinite chains by H-bonds, O—H(BNDA1)···O(DMSO)···H—O(BNDA2). Such behaviour is characteristic for DMSO complexes.[16] Aside from these conventional O—H···O H-bonds there are a number of weak C—H···O type interactions. This particular mode of interaction has given rise to an animated discussion in recent years, mostly because of the uncertainty of the cut-off criteria.[17] Considering the conclusion of Steiner[18] in a recent review devoted to this problem, we follow the so-called 2.8 Å limit that he suggested. More properly, by means of a pair of host–guest interactions O(1)—H···O(1S) and C(1S)—H···O(2), BNDA and DMSO molecules form an eight-membered loop. This host–guest associate incorporated with neighbouring analogous units yield infinite zig-zag chains running along the [101] direction by H-bonding, O(3)—H···O(1S). These chains are incorporated in layers parallel to the *xz* plane by means of weak interactions, C(1S)—H···O(4), C(2S)—H···O(1), C(4)—H···O(4) and C(1S)—H···π-system of the benzene ring C(15)—C(20) (Table 1). The crystal structure appears in the packing of such bimolecular layers (Figure 3). The interaction between the layers is realized by van der Waals contacts.

It is worth noting that in the two different positions the DMSO molecule has completely different interactions with BNDA molecules. In the main position with sof = 0.825 an O atom is tightly fixed by H-bonds (Table 1) and the methyl group C(1S) is located in the host



a)



b)

Figure 1. View of the asymmetric unit of the BNDA·DMSO supramolecular associates without showing the disorder of the DMSO molecule and of the carboxylic group of the BNDA molecule (a) in the α-form 1:1 BNDA·DMSO and (b) the β-form 1:2 BNDA·DMSO complexes, respectively, including atom labelling scheme

pocket surrounded by five BNDA molecules (these host molecules are at a distance of 3.4–3.8 Å). This methyl group is also fixed by three bonds (Table 1). Another methyl group C(2S) has only two host molecules in its vicinity at distances of 3.4 and 3.7 Å and only one hydrogen atom of this methyl group participates in the weak CH_2—H···O interaction (Table 1) that cannot fix this group, have high temperature factors are characteristic of it. On the other hand, the minor occupied other position (sof = 0.175) is favourable for this methyl group because here it is found to be in the region of four BNDA molecules at distances of 3.4–3.8 Å. Furthermore, this

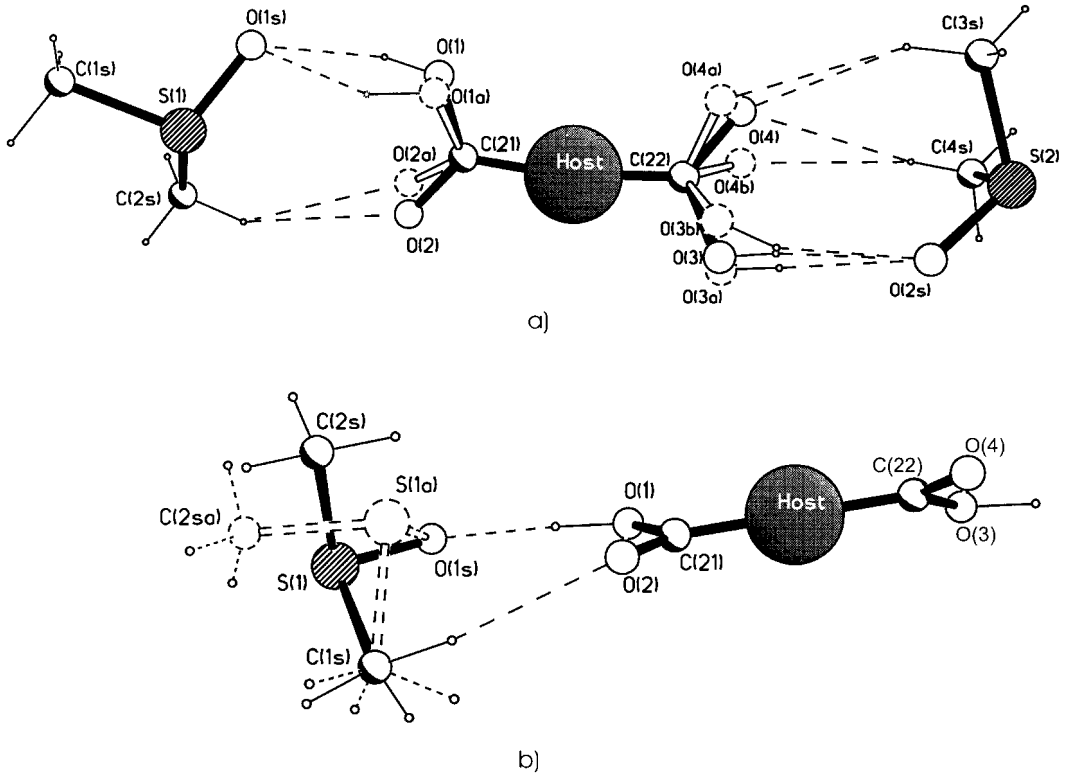


Figure 2. Perspective views of (a) the two- and threefold disordering of the carboxyl groups of the BNDA molecule in the β-form 1:2 BNDA·DMSO complex and (b) the disordering of the DMSO molecule in α-form 1:1 BNDA·DMSO complex with the framework of the BNDA molecules being replaced by spheres

position is favourable for the S atom, making possible a close distance to the carboxyl group of the BNDA (up to 3.0 Å). The O atom and the C(1S) group are in their previous positions. Therefore, in the new position the DMSO molecule (or its all four atom groups) is strongly fixed. Moreover, Fig. 2(b) shows that the new orientation is enantiomeric with the major one with sof = 0.825, which means that it is impossible to come to the minor occupied position if the atom O and the methyl group C(1S) are held fixed. Hence conversion of the ordered crystal species of BNDA·DMSO obtained under ordinary conditions into the disordered crystal species grown at 50 °C is impossible just by heating the ordered crystals. In order to prepare the disordered crystals, the temperature of the crystallization medium (solution) should be increased. Gradually raising of the crystallization temperature might be used in order to shift all guest molecules to the new position in the α-phase if unexpected crystallization of the β-form did not occur at 60 °C.

Crystal structure of the β-form

There are one BNDA molecule and two DMSO molecules in the asymmetric part of the unit cell of the BNDA·DMSO (1:2) β-form complex. These solvent molecules are attached by H-bonds to the carboxyl groups of both halves of the BNDA molecule. The structure of this unit is shown in Fig. 1(b), where only

Table 1. Intermolecular H-bonds and selected weak interactions in the α-form 1:1 BNDA·DMSO complex

Atoms involved	Symmetry	D···A (Å)	D—H (Å)	H···A (Å)	∠D—H···A (°)
O(1)—H(10)···O(1S)	x, y, z	2.643(2)	0.91(3)	1.75(3)	169(3)
O(3)—H(30)···O(1S)	$-0.5+x, 1.5-y, 0.5+z$	2.650(2)	0.86(3)	1.82(3)	164(3)
C(1S)—H(1SA)···O(2)	x, y, z	3.303(4)	0.97(3)	2.38(3)	160(2)
C(1S)—H(1SB)···O(4)	$1+x, y, z$	3.169(3)	0.96(3)	2.68(3)	112(2)
C(1S)—H(1SC)···π(naphtyl)	$1+x, y, z$	3.674	0.96(3)	2.74	145
C(4)—H(4)···O(4)	$-0.5+x, 1.5-y, -0.5+z$	3.488(3)	0.94(2)	2.62(2)	153(2)
C(2S)—H(2SA)···O(1)	$0.5+x, 1.5-y, 0.5+z$	3.400(5)	0.92(4)	2.61(4)	144(3)

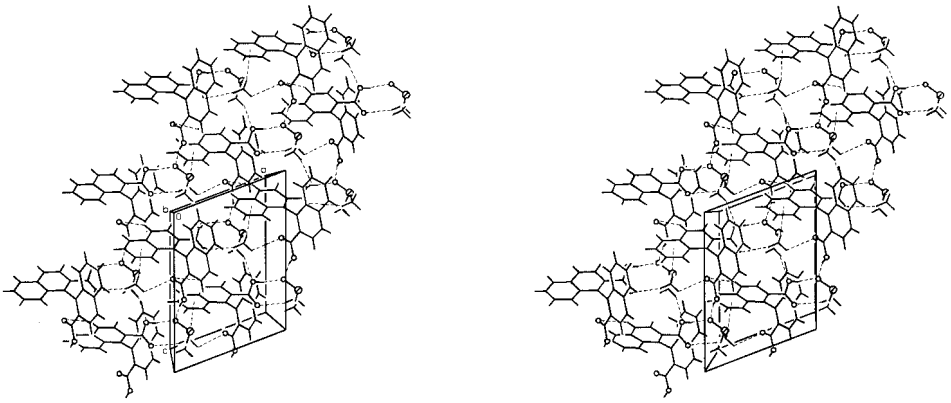


Figure 3. Stereoview of the crystal structure of the α-form 1:1 BNDA·DMSO complex. O and S atoms are indicated as bold dots and hatched circles, respectively. Hydrogen bonds are given as broken lines

major orientations of the disordered groups are represented. As can be seen, the mode of association between the guest and different halves of the BNDA molecule is not the same. While the mode of association of the DMSO molecule **I** is analogous to that found in the α-form structure, *i.e.* two intermolecular interactions close eight-membered loops, the DMSO molecule **II** is oriented relative to the carboxyl group in such a way that the carbonyl oxygen O(4) of the BNDA molecule is located in the middle of the methyl groups being simultaneously involved in the nearly symmetric bonds C(3S)—H···O(4) and C(4S)—H···O(4) showing double acceptor properties. The O(3)—H group is H-bonded to the oxygen atom of the DMSO molecule. These three bonds form two eight-membered loops and one six-membered loop (Table 2).

By translation, for example, along the *x*-axis and further inversion of these 1:2 associates, the DMSO molecules are concentrated in the region consisting of the four solvent molecules and the same amount of host molecules. Here, in the 'solvent region,' DMSO molecules of both types are in contact with each other and with the carboxyl groups to which they are not directly bonded. The latter contact may not be considered an H-bond but only a van der Waals interaction.[18] The DMSO molecules of the different types are associated by C(4S)—H···O(1S) and C(1S)—H···O(2S) bonds. As a consequence of these interactions, a column running in the direction of the *x*-axis and having bimolecular thickness in the direction of the two other axes is formed in its neighbouring 'solvent regions' joined through BNDA molecules. In the direction of the *y*-axis these columns are incorporated by C(7)—H···O(4) bonds, giving rise to the layers in the *xy* plane. The packing of

Table 2. Intermolecular H-bonds and selected weak interactions in the β-form 1:2 BNDA + DMSO complex

Atoms involved	Symmetry	D···A (Å)	D—H (Å)	H···A (Å)	∠D—H···A (°)
O(1)—H(10)···O(1S)	*x*, *y*, *z*	2.605(3)	0.82(3)	1.79(3)	172(3)
C(2S)—H(2SA)···O(2)	*x*, *y*, *z*	3.257(4)	0.95(4)	2.43(4)	145(3)
O(1A)—H(1OA)···O(1S)	*x*, *y*, *z*	2.61(1)	0.82	1.79	174
C(2S)—H(2SA)···O(2A)	*x*, *y*, *z*	3.42(1)	0.95(4)	2.65(4)	139(3)
O(3)—H(30)···O(2S)	*x*, *y*, *z*	2.623(3)	0.71(5)	1.92(6)	173(5)
C(3S)—H(3SA)···O(4)	*x*, *y*, *z*	3.325(6)	0.94(3)	2.48(3)	150(3)
C(4S)—H(4SA)···O(4)	*x*, *y*, *z*	3.439(8)	0.86(4)	2.68(4)	148(3)
O(3A)—H(30A)···O(2S)	*x*, *y*, *z*	2.73(1)	0.82	1.92	169
C(3S)—H(3SA)···O(4A)	*x*, *y*, *z*	3.30(1)	0.94(3)	2.43(4)	155(3)
O(3B)—H(30B)···O(2S)	*x*, *y*, *z*	2.68(1)	0.82	1.91	157
C(4S)—H(4SA)···O(4B)	*x*, *y*, *z*	3.24(1)	0.86(4)	2.44(4)	156(3)
C(7)—H(7)···O(4)	$1-x$, $1-y$, $1-z$	3.191(4)	0.95(3)	2.59(2)	122(2)
C(8)—H(8)···O(4A)	$1-x$, $1-y$, $1-z$	3.39(1)	0.91(2)	2.71(2)	132(2)
C(15)—H(15)···O(4B)	*x*, $1-y$, $1-z$	3.307(7)	0.96(2)	2.70(2)	121(2)
C(4S)—H(4SB)···O(1S)	$-x$, $-y$, $1-z$	3.403(4)	0.96(4)	2.65(4)	136(3)
C(1S)—H(1SC)···O(2S)	$-1+x$, *y*, *z*	3.414(4)	0.85(3)	2.76(3)	136(2)
C(2S)—H(2SC)···O(3B)	$-1+x$, *y*, *z*	3.054(9)	0.87(3)	2.35(3)	138(3)
C(1S)—H(1SA)···O(1A)	$-1-x$, $-y$, $-z$	3.258(9)	0.90(4)	2.57(4)	133(3)

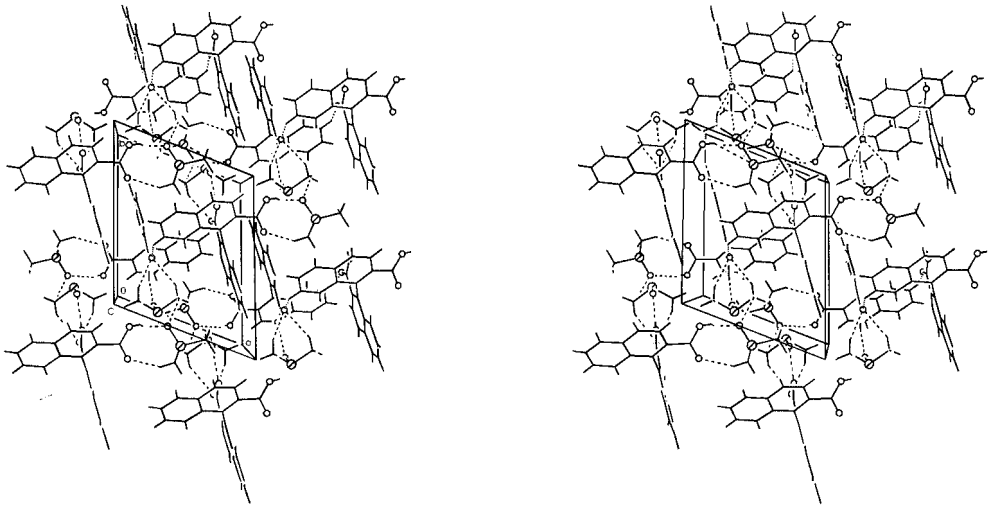


Figure 4. Stereoview of the crystal structure of the β-form 1:2 BNDA·DMSO complex. O and S atoms are indicated as bold dots and hatched circles, respectively. Hydrogen bonds are given as broken lines

these layers with nearly hydrophobic surfaces form the crystal structure of the β-form complex (Fig. 4). This structure results if one takes into account interactions of the major orientations of the disordered carboxyl groups. However, if interactions by the minor orientations of the disordered groups are considered, the interacting pattern within the layer becomes more complicated, making the associates more compact, but the formation of the three-dimensional network does not occur.

The twofold disorder of the —CO(1)O(2)H group does not change the direction of coordinative interactions between BNDA and DMSO molecules. In contrast, in the case of the threefold disorder of the other carboxylic group, it is changed. The carbonyl atom O(4) in the **A** or **B** orientation is located strictly opposite the methyl group of DMSO and has only one C(3S)—H···O(4A) or C(4S)—H···O(4B) bond, respectively, to it instead of the two bonds in the case of the major orientation. The loss of the interaction energy by this bond is compensated for by other C(8)—H···O(4A) or C(15)—H···O(4B) interactions (Table 2).

CONCLUSIONS

In the α-form complexes of BNDA with DMSO, a complicated system of intermolecular interactions is revealed. The oxygen atom of the DMSO molecule shows specific double proton acceptor properties, but in the case of the β-complex as second component of the bond there is a C–H···O interaction instead of the traditional O—H···O bonds. The DMSO molecule tries to form as many H-bonds as possible. For example, all hydrogen atoms of its one methyl group are involved simultaneously in the different interactions with three different partners in the α-form complex. Four different dispositions of the DMSO molecule relative to the carboxyl group of the BNDA molecules giving rise to the four respective host–guest associates are established. Together with conventional O—H···O type H-bonds, more rarely occurring C—H···π, C—H···O and Ar—H···O interactions exist in the crystal structures. The realization of no less than four different types of interactions in each bimolecular complex, components of which are hosts having only carboxylic groups and aprotic solvent, is a characteristic feature of these pseudo-dimorphic complexes.

It is known that disordering takes place because of the requirement for the entropy to be increased. As a rule, the interaction energy with the environment is not changed as a consequence of disordering. We consider that the disorder encountered in both of our structures obtained at relatively high temperatures is the reaction of the crystal to changes in its growing conditions. In order to support crystallization of the clathrate growing at relatively high temperatures, the system should react to the escape of the guest component by its stronger enclathration which occurs as a result of the structure rearrangement. Stronger enclathration means a strong interaction with the environment, especially with the nearest molecules. For this purpose, some of the components will change orientation, *i.e.* a 'new' structure appears relative to the given structure. Superposition of these two structures gives rise to the disordered crystal structure. A more compact association between the host and guest molecules is realized in two ways: through involving of the extra types of host–guest H-bonding appearing as a result of reorientation and by more effective interaction because of optimization of the orientation. In order for these effects to arise there are also two ways: disordering of the guest and disordering of the host. In the case of the α-form complex the DMSO molecules are disordered

Table 3. Crystal data and selected experimental details for the complexes of BNDA with DMSO

Host–guest complex	α-Form	β-Form
Empirical formula	$C_{22}H_{14}O_4 \cdot C_2H_6OS$	$C_{22}H_{14}O_4 \cdot 2C_2H_6OS$
Formula weight	420.46	498.59
Crystal system	Monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	9.694(2)	9.614(2)
b (Å)	17.963(4)	11.743(2)
c (Å)	12.913(3)	12.029(2)
α (°)	90	99.35(3)
β (°)	110.75(3)	93.58(3)
γ (°)	90	110.51(3)
V (Å^3)	2103	1244
Z	4	2
D_c (g cm^{-3})	1.328	1.330
Absorption coefficient (mm^{-1})	0.187	0.253
F (000)	880	524
Crystal size (mm)	0.5 × 0.5 × 0.3	0.5 × 0.4 × 0.2
θ-Range (°)	2.03 to 29.97	1.73 to 29.98
Index ranges	$0 \le h \le 13$, $0 \le k \le 22$, $-17 \le \rho \le 16$	$0 \le h \le 13$, $-16 \le k \le 15$, $-16 \le l \le 16$
Radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
Temperature (K)	293(2)	293(2)
Reflections collected	6309	7652
Independent reflections	5999 [R(int) = 0.0154]	7251 [R(int) = 0.0103]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5074/0/365	6261/7/440
Goodness-of-fit on F^2	1.008	1.053
Final R indices [$I > 2\sigma$ (I)]	$R1$ = 0.054, $wR2$ = 0.1201	$R1$ = 0.053, $wR2$ = 0.1394
R indices (all data)	$R1$ = 0.097, $wR2$ = 0.1448	$R1$ = 0.088, $wR2$ = 0.1627
Largest diff. peak and hole (e Å^{-3})	0.26 and −0.18	0.38 and −0.24

whereas in the β-form complex the disordered molecules are BNDA. Based on results of the present investigation we think that if crystals of the 1:2 β-form BNDA·DMSO complex could be obtained at room temperature and crystals of the 1:1 α-form BNDA·DMSO complex could be obtained at lowest possible temperature, the clathrates should have less disorder or may not have disorder at all.

EXPERIMENTAL

In order to obtain single crystals at the relatively high temperatures, saturated solutions of BNDA in DMSO were prepared under ambient conditions and 1–2 drops of water were added before inserting of samples in the thermostat at 50 and 60 °C. Colourless and prism-shaped crystals were grown during evaporation of the solvent. Single crystals of α- and β-form complexes with dimensions 0.5 × 0.5 × 0.3 and 0.5 × 0.4 × 0.2 mm, respectively, were used for all measurements on an Enraf-Nonius CAD-4 diffractometer. The unit cell parameters were determined by a least-squares fitting of the setting angles of 25 reflections (θ in the range 12–15°). Crystal data and selected experimental details are shown in Table 3.

Reflection intensities were measured with graphite monochromatized Mo Kα radiation. The structure was solved by direct methods using the program SHELXS-86.[19] All non-hydrogen atoms and disorder of the DMSO molecules and the carboxyl groups in the α- and β-form complexes, respectively, were located from the first E-map. The refinement of the structures was carried out with the program SHELXL-93[20] using its facilities for disordering structures.

All hydrogen atoms of the molecules were found from difference syntheses and refined with isotropic vibration parameters in both compounds. H-atoms of the disordered OH groups in the β-form complex and disordered solvent methyl group hydrogens in the α-form having small sof were placed at the calculated positions.

Carboxylic groups disordered around two positions in the β-form and DMSO molecules in the α-form were restrained by equating the sof sum to unity using free variables, whereas in the case of carboxylic groups disordered in three positions in the β-form complex the analogous restraint was applied by involving the SUMP and PART instructions in SHELXL-93.

Supplementary data

The tables of final fractional atomic coordinates, bond lengths and angles involving all the non-hydrogen and hydrogen atoms and anisotropic displacement parameters for the non-hydrogen atoms have been deposited as supplementary data at the Cambridge Crystallographic

Data Centre. Lists of the observed and calculated structure factors and the anisotropic displacement parameters for the non-hydrogen atoms may be obtained from the authors (B.T.I. and E.W.) on request.

Acknowledgements

E.W. thanks the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie for financial support. B.I. is also grateful to the DFG for providing a travel grant to Germany. K.B. thanks the Alexander von Humboldt Foundation for a scholarship. This work is part of the Graduate School Programme (GRK 208) of the TU Bergakademie Freiberg supported by the DFG.

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