Polymorphism of Inclusion Complexes and Unsolvated Hosts. IV. Dimorphism of the Acetone Host–Guest Complex of Dianilinegossypol. Structures of the α- and β-Phase Complexes

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Abstract. Crystal structures of the α- and β-phase inclusion complexes of dianilinegossypol with acetone obtained at 20° and 30 °C, respectively, have been determined by X-ray structure analysis. Crystal data of the α-phase complex are: $C_{42}H_{40}O_6N_2 \cdot 2C_3H_6O$, orthorhombic, space group *Pccn*, $a = 29.501(9)$, $b = 10.866(2)$, $c = 13.756(3)$ Å, $V = 4409(1)$ Å^3, $Z = 4$, $D_x = 1.18$ g cm^{-3}. The structure has been refined to a final R value of 0.117 for 1401 observed reflections. The host–guest ratio for the β-phase complex is the same (1 : 2) and the crystals are monoclinic, space group $C2/c$, $a = 28.352(6)$, $b = 11.836(2)$, $c = 13.196(1)$ Å, $\beta = 93.05(1)°$, $V = 4422(2)$ Å^3, $Z = 4$, $D_x = 1.18$ g cm^{-3}. The structure has been refined to a final R value of 0.077 for 1414 observed reflections.

In both phases molecules of dianilinegossypol form hydrogen-bonded ribbons by O(4)—H· · ·O(3) H-bonds. Phases are determined by the same structural motif. In the β-phase complex the cages are in the form of prisms but in the α-phase clathrate they undergo a modification by shrinking in two directions and widening in one. Molecules of acetone are hydrogen bonded to the host molecules via a O(1)—H· · ·O(G) bond and are accommodated in cavities for both complexes, i.e. both phases are cryptate-type inclusion complexes.

Key words: Crystal structure, X-ray crystallography, H-bond, dianilinegossypol, α- and β-phase of the host–guest complex.

1. Introduction

Gossypol and its condensation product with aniline, named dianilinegossypol, which is a Schiff's base type derivative, are versatile hosts, capable of including numerous types of guest species [1–3]. Moreover, they are able to form more than one host–guest complex with the same guest depending on the crystallization conditions. Our interest is in establishing structural differences between clathrates obtained under various conditions, e.g. at different temperatures. In the case of the dichloromethane complex of gossypol a change of temperature over a small range gives rise to three inclusion complexes which are characterized by different systems

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of host–host hydrogen bonding [4]. Depending on temperature, dianilinegossypol forms with ethylacetate two types of 1 : 1 host–guest complexes having the same type of host–host association. The difference between the low (α-phase) and high (β-phase) temperature complexes is in the packing mode of the associations [5].

Acetone, which like ethylacetate is an aprotic solvent, also gives two new host–guest complexes relating to different isostructural groups of the dianilinegossypol clathrates. It is interesting that these 1 : 2 host–guest complexes are crystallized in the more highly symmetric space groups. This paper is devoted to further investigations of rearrangements in host–guest structures occurring as a result of temperature change.

2. Experimental

Needle-shaped single crystals of the α-phase and prism-shaped single crystals of the β-phase complexes were obtained from solutions of dianilinegossypol in acetone by slow evaporation at $20°$ and $30°$, respectively. Unit-cell parameters were determined on a Syntex $P2_1$ diffractometer by least-squares fitting of the setting angles of 15 reflections (2θ in the range 25–40°).

Crystal data: *α-phase:* $C_{42}H_{40}O_6N_2 \cdot 2C_3N_6O$, orthorhombic, space group $Pccn$, $a = 29.501(9)$, $b = 10.866(2)$, $c = 13.756(3)$ Å, $V = 4409(1)$ Å^3, $Z = 4$, $D_x = 1.18$ g cm^{-3}.

β-phase: $C_{42}H_{40}O_6N_2 \cdot 2C_3H_6O$, monoclinic, space group $C2/c$, $a = 28.352(6)$, $b = 11.836(2)$, $c = 13.196(1)$ Å, $\beta = 93.05(1)°$, $V = 4422(2)$ Å^3, $Z = 4$, $D_x = 1.18$ g cm^{-3}.

The intensities of the reflections were measured with graphite monochromatized CuK_α radiation up to $2\theta_{max} = 120°$. No significant intensity variation was observed for two standard reflections monitored after each group of 100 reflections. Data were corrected for Lorentz and polarization effects but not for absorption. Out of 3504 measured reflections 1401 had $I > 2.5\sigma(I)$ for the α-phase and out of 2655 measured reflections 1414 had $I > 2\sigma(I)$ for the β-phase and were used for further calculations. The structures were solved by direct methods with the program SHELXS-86 [6]. Dianilinegossypol and acetone molecules were located on the 'best' E map. The structures were refined first with isotropic and then with anisotropic thermal parameters by least-squares methods using the program SHELX93 [7]. In the case of the α-phase complex hydrogen atoms were placed at the calculated positions. Hydrogen atom positions of the β-dimorph were determined from the ΔF maps and their positional and isotropic thermal parameters were included in the refinement. Final values of R and WR are 0.117 and 0.118 for the α-phase and 0.077 and 0.079 for the β-phase, respectively.

Table I. Atom coordinates ($\times 10^4$) and temperature factors
($\text{Å}^2 \times 10^3$).

Atom	x	y	z	U^*
(a) α-phase				
C(1)	6998(4)	1671(12)	5809(9)	54(5)
C(2)	7248(3)	2511(14)	6341(9)	53(5)
C(3)	7016(4)	3372(13)	6913(10)	68(6)
C(4)	6549(4)	3339(13)	6966(10)	71(6)
C(5)	5792(4)	2456(13)	6514(11)	70(6)
C(6)	5572(4)	1646(14)	6020(12)	76(6)
C(7)	5764(4)	767(12)	5372(10)	60(5)
C(8)	6252(4)	747(12)	5241(9)	52(5)
C(9)	6517(3)	1611(11)	5804(9)	46(4)
C(10)	6296(3)	2458(13)	6423(10)	57(5)
C(11)	7269(4)	4338(14)	7523(12)	112(8)
C(12)	6428(4)	−91(14)	4576(11)	64(5)
C(13)	5539(4)	3413(17)	7128(16)	115(9)
C(14)	5210(6)	4205(16)	6612(18)	182(14)
C(15)	5310(6)	2751(22)	7983(13)	177(13)
C(16)	6328(5)	−1722(16)	3442(13)	89(7)
C(17)	6769(5)	−2194(15)	3433(17)	134(11)
C(18)	6903(6)	−3097(18)	2761(16)	128(10)
C(19)	6606(7)	−3541(21)	2084(16)	154(12)
C(20)	6177(7)	−3150(20)	2113(16)	153(12)
C(21)	6G36(5)	−2235(18)	2735(14)	123(10)
O(1)	7213(2)	851(9)	5239(8)	70(4)
O(2)	5513(2)	1(9)	4915(7)	83(4)
N(1)	6187(3)	−851(11)	4098(8)	66(5)
O(4)	5097(2)	1540(8)	6066(7)	79(4)
O(1a)	6929(5)	−5352(26)	4791(16)	318(16)
C(1a)	6596(7)	−5248(26)	4636(21)	145(13)
C(2a)	6377(16)	−6038(49)	3924(32)	341(38)
C(3a)	6226(13)	−4467(33)	4959(28)	353(25)

3. Results and Discussion

Atom coordinates and equivalent thermal parameters are given in Table I. The hydrogen atom parameters, anisotropic thermal parameters and structure factors are in the Supplementary Material. The numbering scheme of dianilinegossypol and guest molecules are shown in Figure 1.

Table I. Continued.

Atom	x	y	z	U^*
(b) β-phase				
C(1)	4504(3)	1156(6)	6778(5)	40(3)
C(2)	4736(3)	399(6)	7447(5)	41(3)
C(3)	4466(3)	−331(7)	7984(6)	53(4)
C(4)	3992(4)	−309(7)	7856(6)	58(4)
C(5)	3227(4)	423(6)	7087(6)	56(4)
C(6)	3011(3)	1067(7)	6363(6)	55(4)
C(7)	3264(3)	1840(7)	5753(6)	58(4)
C(8)	3761(3)	1952(6)	5893(5)	44(3)
C(9)	4006(3)	1198(6)	6624(5)	36(3)
C(10)	3743(3)	437(6)	7202(6)	45(3)
C(11)	4691(3)	−1159(10)	8753(8)	104(5)
C(12)	3979(3)	2789(6)	5340(5)	46(3)
C(13)	2931(4)	−340(11)	7724(8)	94(5)
C(14)	2581(4)	308(11)	341(8)	126(6)
C(15)	2694(5)	−1300(10)	7131(12)	150(7)
C(16)	3960(4)	4297(7)	4081(6)	53(4)
C(17)	3655(3)	4962(8)	3495(7)	74(4)
C(18)	3833(4)	5806(9)	2903(8)	97(5)
C(19)	4311(4)	6029(8)	2923(7)	78(4)
C(20)	4590(3)	5351(9)	3513(7)	83(4)
C(21)	4434(4)	4487(7)	4083(6)	61(4)
O(1)	4771(2)	1903(4)	6269(3)	54(2)
N(1)	3758(2)	3440(5)	4665(5)	54(3)
O(3)	3016(2)	2428(6)	5101(5)	88(3)
O(4)	2535(2)	1096(5)	6172(4)	71(3)
O(1a)	555(4)	2756(12)	132(9)	213(7)
C(1a)	896(6)	2594(17)	−263(12)	137(9)
C(2a)	966(5)	1885(12)	−1112(10)	173(9)
C(3a)	1317(6)	3213(14)	87(11)	197(11)

$^* U = \frac{1}{3} \sum \sum U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$

3.1. MOLECULAR STRUCTURE

In contrast to the two phases of the dianilinegossypol host–guest complex with ethylacetate, an intrinsic symmetry of the host molecule is retained in the case of the acetone complexes. It should be noted that the intrinsic symmetry of the gossypol and its derivative molecules is C_2 and a twofold axis is situated perpendicular to the C(2)—C(2′) bond. Among clathrates of gossypol itself a host molecule lies on the twofold axis of the crystal structure only in the case of the 1,4-dioxane complex [8].
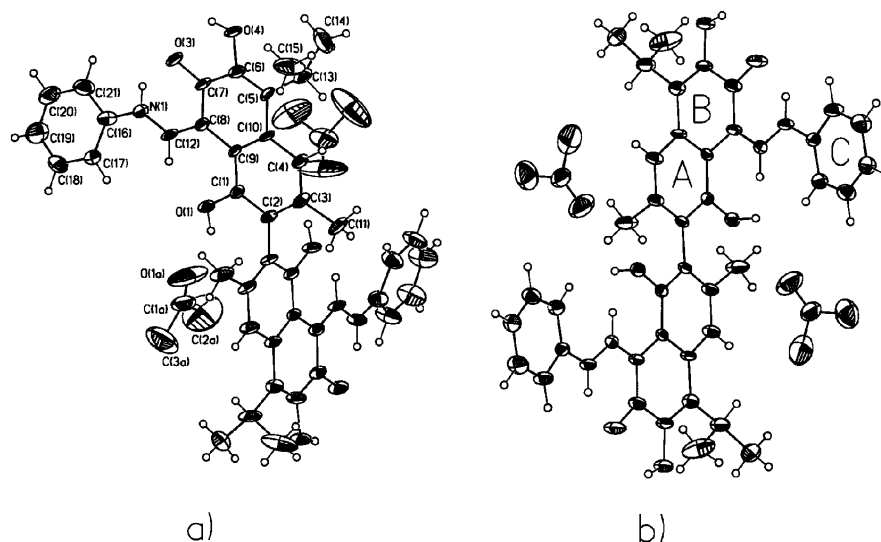
Figure 1. The dianilinegossypol molecule in the α-phase (a) and β-phase (b) complexes and the numbering scheme of the molecule.

Table II. Intramolecular H-bonds in α- (a) and β-phase (b) complexes (hydrogen atoms of the α-phase are placed at calculated positions).

H-bond	D$\cdots$A (Å)	D—H (Å)	H$\cdots$A (Å)	<D—H$\cdots$A($^\circ$)
(a) O(4)—H$\cdots$O(3)	2.61	0.85	2.10	117
N(1)—H$\cdots$O(3)	2.46	0.90	1.72	138
(b) O(4)—H$\cdots$O(3)	2.55	0.73	2.09	122
N(1)—H$\cdots$O(3)	2.51	1.11	1.64	146

Thus the asymmetric part of the unit-cell has only a half of the host molecule. Dianilinegossypol molecules are in a quinoid tautomeric form. The dihedral angle between the least-squares planes of the naphthyl moieties is equal to 81.5 and 92.7° and the aromatic rings of the aniline molecules are inclined to the planes of the naphthyl moieties by 20.8 and 4.4° in the α- and β-phase complexes respectively. The hydrogen atom of the isopropyl group is oriented towards the hydrogen atom on carbon atom C(4) in both structures.

There are two systems of hydrogen bonds in the molecule. H-bonds O(3)...H—N(1) closes the 6-membered ring C(7)—C(8)—C(12)—N(1)—H...O(3) while the other H-bond, O(4)—H...O(3), forms the 5-membered ring C(6)—C(7)—O(3)...H–O(4) (Table II). Lengths and angles of the intramolecular H-bonds of the β-phase complex are in good agreement with those observed in other dianilinegossypol host–guest complexes [5, 9, 10].

Table III. Intermolecular H-bonds in α- (a) and β-phase (b) complexes (hydrogen atoms of the α-phase are placed at calculated positions).

H-bond	O$\cdots$O (Å)	O—H (Å)	H$\cdots$O (Å)	<O—H$\cdots$O ($^\circ$)
(a) O(4)—H$\cdots$O(3)^{i}	2.81	0.85	2.04	148
O(1)—H$\cdots$O(1a)	2.66	0.85	1.94	142
(b) O(4)—H$\cdots$O(3)^{ii}	2.83	0.73	2.10	145
O(1)—H$\cdots$O(1a)	2.77	0.63	2.40	121

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $0.5 - x, 0.5 - y, 1 - z$.
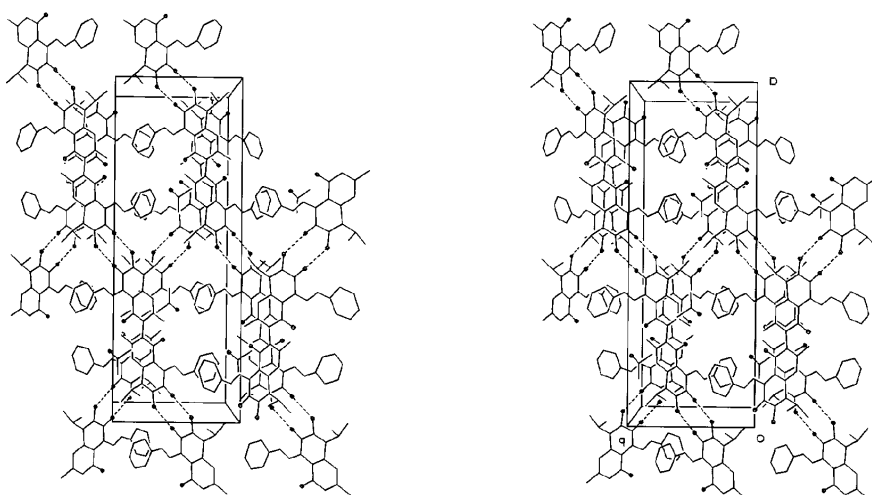
Figure 2. Structure of the α-phase complex.

3.2. CRYSTAL STRUCTURE

In the α-phase complex of dianilinegossypol with acetone, host molecules lie on twofold axes which are parallel to the c-direction. Dianilinegossypol molecules are incorporated into ribbons extended in the [101] direction by means of a pair of centrosymmetric O(4)—H$\cdots$O(3) H-bonds (Table III). As a result of packing of these ribbons a centrosymmetric cage capable of including two acetone molecules is formed (Figure 2).

Figure 3 shows how cages in the clathrate structure are formed. Each cage is formed between four pairs of host molecules, i.e. four ribbons. Within pairs, host molecules are associated by centrosymmetric H-bonds O(4)—H. . . O(3). The pair of molecules **III + IV** is obtained from the **I + II** pair by translation along the b-axis (Figure 3a). Similarly, as a result of translation along the direction perpendicular to the c-axis a pair of molecules **VII + VIII** is obtained from the **V + VI** pair (Figure 3b).

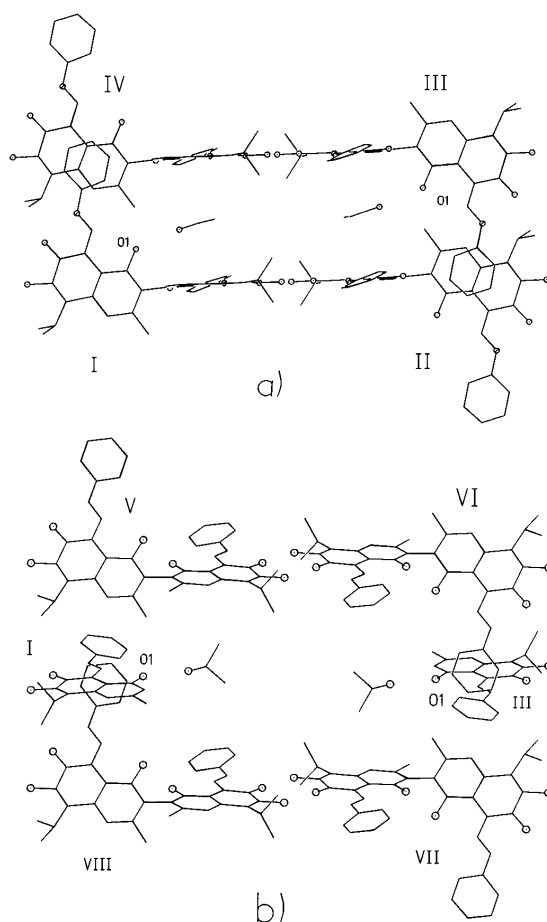*Figure 3.* Formation of the cages in the α-phase complex as a result of the translation of ribbons in the direction of the b-axis (a) and the c-axis (b).

Acetone molecules included in the cages are H-bonded with the O(1)—H groups of dianilinegossypol molecules (AB-half) and the plane of the guest molecule (plane through nonhydrogen atoms of acetone molecule) is nearly parallel to the mean plane of the A′B′-naphthyl fragment (dihedral angle is equal to 14.6°). As the cage is centrosymmetric we will carry out our discussion only for one crystallographically independent half of the cage. Since the acetone molecule lies on the A′B′-naphthalene moiety of the host molecule, the latter will be considered as the floor of the cage. The ceiling of the cage is the aniline ring of molecule **IV**. The aniline ring of molecule **V** and the AB-naphthalene moiety of molecule **VIII** are the walls of the cage (Figure 3b). The aromatic methyl groups of molecule **IV** and the O(1)—H group of molecule **I** close the cage in the a-direction. Notice that acetone molecules are not in immediate contact inside the cage. The hydrophobic
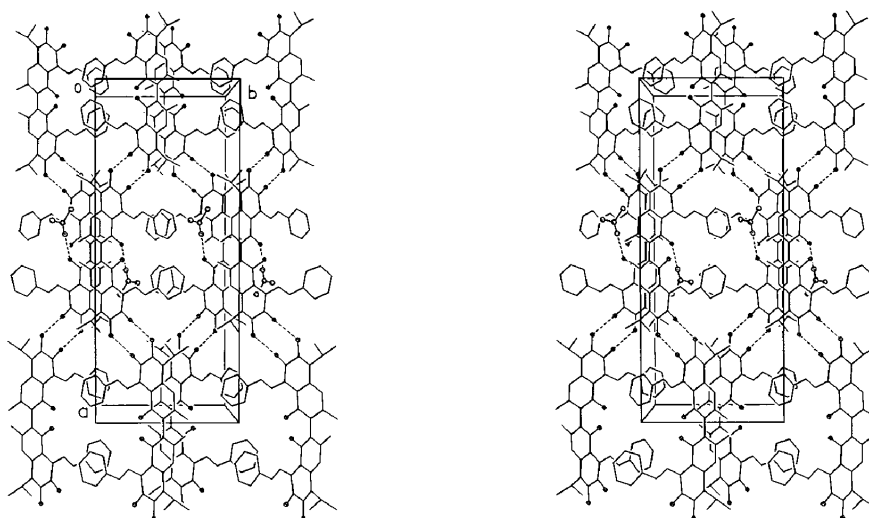
Figure 4. Structure of the β-phase complex.

parts of the acetone molecule, i.e. its methyl groups are in van der Waals interaction with the isopropyl groups of molecules **I** and **IV**. Taking this into account instead of speaking about a centrosymmetric cage including two guest molecules, there is good reason to consider a separate cage accommodating only one acetone molecule.

As a result of slightly raising the crystallization temperature a new clathrate phase of dianilinegossypol with acetone is obtained. Here the symmetry of the crystals is lowered from orthorhombic to monoclinic and the unit cell dimensions of the crystal are approximately retained. This situation means that the structural motif is conserved during the thermotropic phase transition. The results of the structure determination of the β-phase complex confirm this assumption.

As the motif of the structures is the same in both phases all details of the crystal structure, i.e. the mode of formation of ribbons and cages are retained in the case of the β-phase (Figure 4). The main difference is in the orientation of the acetone molecules inside the cage, which, probably serves as the main reason for the symmetry lowering. In β-phase clathrates the plane of the acetone molecule is situated almost perpendicular (85.1°) to the plane of the A′B′- naphthyl fragment of molecule **I** (Figure 5). It is apparent that the floor and ceiling of the cage serve as its walls and *vice versa*.

The inclusion of acetone molecules between two neighboring ribbons of host molecules forces the ribbons apart. This is confirmed by the increased value of the b-translation by 1 Å. Reorientation of the acetone molecule inside the cage results in a decrease of the c-translation value by nearly 0.5 Å and in shrinking of the cage in the a-direction. In other words, in the β-phase complex the cages which existed in the α-phase clathrate in the form of prisms undergo a modification by shrinking
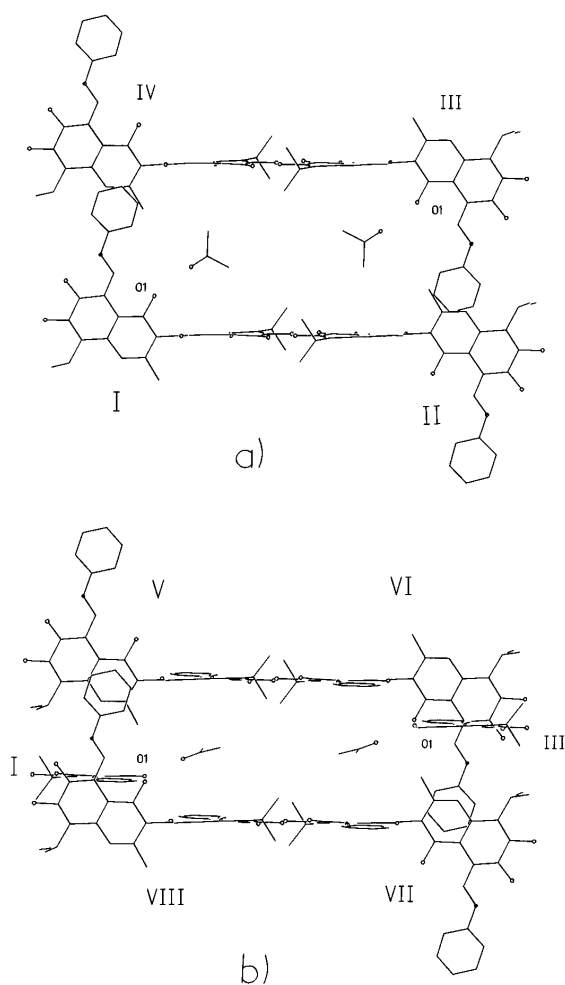
Figure 5. Formation of the cages in the β-phase complex as a result of the translation of ribbons in the direction of the b-axis (a) and the c-axis (b).

in two directions and widening in one. It is likely that cages of such constitutions could not be supported by the *Pccn* space group considered above.

Flat molecules such as methyl acetate, acetyl acetone and methylethylketone form host–guest complexes with dianilinegossypol related to the α-phase. Nonplanar or voluminous molecules like chloroform and dimethylformamide give β-phase type complexes [3]. Up to now dimorphism has been observed only for acetone, probably because of its special shape, which favours both types of orientations inside the cages to the same extent. This confirmation is supported by simultaneous crystallization from solutions of dianilinegossypol in acetone single crystals of both phases at intermediate temperatures, for example, at 24–26 °C.

Thus the host–guest complex of dianilinegossypol with acetone is characterized by dimorphism. The phases are determined by the same structural motif and they are cryptate type inclusion compounds.

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