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Inclusion Complexes of the Natural Product Gossypol. Crystal Structures of Gossypol Complexes with Benzene and Chloroform as Guests

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Abstract. The crystal structures of the lattice inclusion complexes of gossypol with benzene and chloroform have been determined by X-ray structure analysis. The crystals of $(C_{30}H_{30}O_8)_2 \cdot C_6H_6$ (GPBNZ) are triclinic, space group $P\bar{1}$, $a = 11.241(3)$, $b = 14.986(4)$, $c = 17.380(4)$ Å, $\alpha = 98.89(2)$, $\beta = 99.86(2)$, $\gamma = 98.91(2)°$, $V = 2800(2)$ Å^3, $Z = 2$, $D_x = 1.32$ g cm^{-3}, $\mu(\mathrm{Cu}K_\alpha) = 7.35$ cm^{-1}. The structure has been refined to a final R value of 0.050 for 6146 observed reflections. The crystals of $C_{30}H_{30}O_8 \cdot CHCl_3$ (GPCLF) are monoclinic, space group $C2/c$, $a = 28.464(4)$, $b = 8.948(1)$, $c = 26.480(4)$ Å, $\beta = 108.93(2)°$, $V = 6380(2)$ Å^3, $Z = 8$, $D_x = 1.33$ g cm^{-3}, $\mu(\mathrm{CuK}\alpha) = 30.42$ cm^{-1}. The structure has been refined to a final R value of 0.100 for 1980 observed reflections.

GPCLF forms an intercalate-type structure and GPBNZ a clathrate-type structure. There are, however, some similarities in the packing mode of the host molecules in these two structures. On a basis of comparison of the crystal packing of GPCLF and GPBNZ one can postulate that in the desorption process of the intercalate-type GPCLF complex an intermediate clathrate structure of the GPBNZ-type should be formed.

Key words. Crystal structure, X-ray crystallography, gossypol, inclusion complexes.

Supplementary Data relating to this article have been deposited with the British Library as Supplementary Publication No. SUP 82091 (37 pages).

1. Introduction

In a series of previous publications we have reported that gossypol (1,1′,6,6′,7,7′-hexahydroxy-5,5′diisopropyl-3,3′dimethyl[2,2′-binaphthalene]-8,8′-dicarboxaldehyde) is a very versatile host forming lattice inclusion compounds with a large number of polar and nonpolar organic guest molecules [1–5]. In this paper we present the crystal structure of the 1 : 1 gossypol : chloroform inclusion complex which was first obtained by Adams *et al.* [6] and characterized then as a polymorphic modification of gossypol with m.p. 199°C. The structure of the 1 : 1 gossypol : iso-valeric acid complex, which is isostructural with the abovementioned complex, has already been published [5]. It has been shown that inclusion complexes of this type form an intercalate-type structure with the layers of host molecules separated by the layers of guest molecules. The second lattice inclusion complex described in

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this paper, i.e. 2 : 1 gossypol : benzene, belongs to a new class of inclusion complexes of gossypol. The following abbreviations are used throughout the text: GPCLF for gossypol : chloroform and GPBNZ for gossypol : benzene.

2. Experimental

2.1. CRYSTAL STRUCTURE DETERMINATION OF GPBNZ

Single crystals of the gossypol : 0.5 benzene complex were obtained by slow evaporation of a gossypol solution in benzene. A specimen of approximate dimensions of 0.3 × 0.3 × 0.4 mm was used for measurements on a Syntex $P2_1$ diffractometer. Lattice parameters were determined by a least-squares fitting of the setting angles of 15 reflections (2θ in range 16 to 30°).

The crystal data are as follows: $(C_{30}H_{30}O_8)_2 \cdot C_6H_6$, triclinic, space group $P\bar{1}$, $a = 11.241(3)$, $b = 14.986(4)$, $c = 17.380(4)$ Å, $\alpha = 98.89(2)$, $\beta = 99.86(2)$, $\gamma = 98.91(2)°$, $V = 2800(2)$ Å, $Z = 2$, $D_x = 1.32$ g cm^{-3}, $\mu(\mathrm{Cu}K_\alpha) = 7.35$ cm^{-1}, $T = 294$ K.

Intensities of reflections were measured with graphite monochromatized CuK_α radiation ($\lambda = 1.54178$ Å) to $2\theta_{\max} = 120°$. No significant intensity variation was observed for 2 standard reflections monitored after each group of 100 reflections. Data were corrected for Lorentz and polarization effects but not for absorption. Out of 8256 measured reflections 6146 had $I > 1.5\sigma(I)$ and those were designated as observed. The structure was solved by direct methods with the program MULTAN80 [7] and refined first with isotropic and then with anisotropic temperature factors by least-squares methods using the program SHELX76 [8]. The hydrogen atoms of the hydroxyl groups and methyl groups at C(3) and C(13) were located on a ΔF map. The remaining hydrogen atoms were placed in calculated positions [d(C—H) = 1.08 Å]. The positional parameters and isotropic temperature factors of the H atoms located on a ΔF map were allowed to vary during the refinement; for the remaining H atoms only temperature factors were refined. An empirical isotropic extinction parameter x was used to correct F_c according to $F' = F_c(1 - xF_c^2/\sin\theta)$; x converged at $18(3) \times 10^{-8}$. Final values of R and wR are 0.050 and 0.059, respectively. The weighting scheme used was $w = k/[\sigma^2(F_0) + 0.0002F_0^2]$. In the final ΔF map, calculated after the last cycle of refinement, the maximum and minimum peaks were 0.29 and -17 e Å^{-3}, respectively.

2.2. CRYSTAL STRUCTURE DETERMINATION OF GPCLF

Single crystals of the gossypol : chloroform complex were obtained by slow evaporation of a gossypol solution in chloroform. A specimen of approximate dimensions of 0.05 × 0.1 × 0.2 mm was used for measurements on a Syntex $P2_1$ diffractometer. Lattice parameters were determined by a least-squares fitting of the setting angles of 15 reflections (2θ in range 11 to 25°).

The crystal data are as follows: $C_{30}H_{30}O_8 \cdot CHCl_3$, monoclinic, space group $C2/c$, $a = 28.464(4)$, $b = 8.948(1)$, $c = 26.480(4)$ Å, $\beta = 108.93(2)°$, $V = 6380(2)$ Å^3, $Z = 8$, $D_x = 1.33$ g cm^{-3}, $\mu(\mathrm{Cu}K_\alpha) = 30.42$ cm^{-1}, $T = 292$ K.

Intensities of reflections were measured with graphite monochromatized CuK_α radiation ($\lambda = 1.54178$ Å) to $2\theta_{\cdot \max} = 115°$. The intensity of 2 standard reflections, monitored after each group of 100 reflections, fluctuated within $\pm 10\%$. The data were not corrected for these fluctuations. Corrections for Lorentz and polarization factors were applied, but not for absorption. Out of 4493 measured reflections 1980 had $I > 1.5\sigma(I)$.

GPCLF is isostructural with the gossypol: iso-valeric acid complex [5]. The coordinates of the gossypol molecule from that structure were used to calculate a ΔF map. The peak pattern in this ΔF map indicated that the chloroform molecule is disordered. The resultant pattern emerging from the ΔF map shows the chloroform molecule disordered around the CH bond, however, this disorder can be either static or dynamic. Three peaks corresponding to one orientation of the chloroform molecule were approximately twice as intense as the remaining peaks and therefore this orientation, called A, was given an occupancy factor of 0.4. Three other orientations (B, C and D) were found and they were given an occupancy factor of 0.2 each.

The structure was refined by least-squares methods, using the program SHELX76 [8], with isotropic temperature factors for the chloroform chlorine and carbon atoms and with anisotropic temperature factors for the non-hydrogen atoms of the host. The hydroxyl group hydrogen atoms were not found on a ΔF map. The remaining hydrogen atoms were placed in calculated positions [d(CH) = 1.08 Å]. The chloroform molecule was refined in all orientations as a rigid group with the Cl—Cl distance fixed at 2.85 Å. In orientation A the C—Cl distance was also fixed at 1.76 Å. Final values of R and wR are 0.10 and 0.12, respectively. The weighting scheme used was $w = k/[\sigma^2(F_0) + 0.0005F_0^2]$. In the final ΔF map, calculated after the last cycle of refinement, the maximum and minimum peaks were 0.50 and $-0.40\ e$ Å^{-3}, respectively.

The scattering factors used in the calculations were those included in SHELX76 [8]. Drawings were prepared with the programs PLUTO [9] and ORTEP [10].

3. Results and Discussion

The atomic parameters are given in Table I. Bond lengths, bond angles, equations of the least-squares planes of the naphthyl moieties and deviations of the atoms from those planes, hydrogen atom parameters, anisotropic thermal parameters and structure factors are in the Supplementary Material. The numbering scheme of gossypol and the guest molecules is shown in Figure 1.

3.1. MOLECULAR STRUCTURE

There are two independent molecules, A and B, in the asymmetric part of the unit cell in GPBNZ and one molecule in the asymmetric part in GPCLF. Bond lengths and angles of the host are in good agreement with the values observed in the other gossypol inclusion complexes. In the structures described here gossypol is in the aldehyde form, the only one found for gossypol in the crystalline state up to now. Due to the restricted rotation around the C(2)—C(12) bond two atropoisomers, *R*

Table I. Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3}\sum_{i}\sum_{j} U_{ij}a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

a. gossypol : 0.5 benzene

Atom	x/a	y/b	z/c	U_{eq}
C(1A)	−0.0130(3)	0.3484(2)	0.0921(2)	0.040(1)
C(2A)	−0.0039(3)	0.2559(2)	0.0663(2)	0.042(1)
C(3A)	0.0960(3)	0.2085(2)	0.0053(2)	0.049(1)
C(4A)	0.1807(3)	0.2570(2)	−0.0265(2)	0.048(1)
C(5A)	0.2630(3)	0.4000(2)	−0.0373(2)	0.043(1)
C(6A)	0.2442(3)	0.4935(2)	−0.0153(2)	0.044(1)
C(7A)	0.1471(3)	0.5427(2)	0.0473(2)	0.043(1)
C(8A)	0.0615(3)	0.4984(2)	0.0867(2)	0.040(1)
C(9A)	0.0714(3)	0.4009(2)	0.0608(2)	0.038(1)
C(10A)	0.1723(3)	0.3522(2)	−0.0009(2)	0.040(1)
C(11A)	−0.2002(3)	0.1946(2)	0.0771(2)	0.041(1)
C(12A)	−0.0946(3)	0.2040(2)	0.1050(2)	0.043(1)
C(13A)	−0.0702(3)	0.1619(2)	0.1689(2)	0.055(2)
C(14A)	−0.1518(3)	0.1116(2)	0.2009(2)	0.052(2)
C(15A)	−0.3396(3)	0.0437(2)	0.2069(2)	0.046(1)
C(16A)	−0.4409(3)	0.0331(2)	0.1760(2)	0.058(2)
C(17A)	−0.4696(3)	0.0751(2)	0.1118(2)	0.055(2)
C(18A)	−0.3936(3)	0.1273(2)	0.0755(2)	0.045(1)
C(19A)	−0.2847(3)	0.1415(2)	0.1070(2)	0.041(1)
C(20A)	−0.2591(3)	0.0994(2)	0.1720(2)	0.041(1)
C(21A	0.1129(5)	0.1059(3)	−0.0233(3)	0.081(2)
C(22A)	−0.0288(3)	0.5567(2)	0.1518(2)	0.059(2)
C(23A	0.3762(3)	0.3481(2)	−0.0987(2)	0.053(2)
C(24A)	0.3637(3)	0.3586(3)	−0.1836(2)	0.072(2)
C(25A)	0.4965(3)	0.3736(3)	−0.0780(3)	0.078(2)
C(26A)	0.0434(5)	0.1722(5)	0.2021(4)	0.084(2)
C(27A)	−0.4290(3)	0.1614(2)	0.0073(2)	0.064(2)
C(28A)	−0.3129(3)	−0.0039(2)	0.2748(2)	0.051(1)
C(29A)	−0.4164(3)	0.0251(3)	0.3486(2)	0.075(2)
C(30A)	−0.2809(4)	−0.1082(2)	0.2497(2)	0.080(2)
O(1A)	−0.1079(2)	0.3958(2)	0.1522(2)	0.058(1)
O(2A)	−0.0320(2)	0.6408(2)	0.1724(2)	0.069(1)
O(3A)	0.1450(2)	0.6331(2)	0.0673(2)	0.054(1)
O(4A)	0.3229(2)	0.5443(2)	−0.0512(2)	0.056(1)
O(5A)	−0.2264(2)	0.2386(2)	0.0158(2)	0.056(1)
O(6A)	−0.5247(2)	0.1508(2)	−0.0158(2)	0.079(1)
O(7A)	−0.5743(2)	0.0592(2)	0.0894(2)	0.078(1)
O(8A)	−0.5224(3)	−0.0184(2)	0.2060(2)	0.092(2)
C(1B)	−0.2229(3)	0.9043(2)	0.4812(2)	0.043(1)
C(2B)	−0.2258(3)	0.8125(2)	0.4728(2)	0.047(1)
C(3B)	−0.1325(3)	0.7488(2)	0.4163(2)	0.058(2)
C(4B)	−0.0410(3)	0.7816(2)	0.3722(2)	0.059(1)
C(5B)	0.0645(3)	0.9065(2)	0.3344(2)	0.050(1)
C(6B)	0.0741(3)	0.9967(2)	0.3507(2)	0.047(1)
C(7B)	−0.0176(3)	1.0623(2)	0.4066(2)	0.045(1)
C(8B)	−0.1214(3)	1.0371(2)	0.4484(2)	0.042(1)
C(9B)	−0.1296(3)	0.9410(2)	0.4378(2)	0.042(1)

Table I. (continued)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
C(10B)	−0.0359(3)	0.8764(2)	0.3812(2)	0.047(1)
C(11B)	−0.3146(3)	0.7657(2)	0.5986(2)	0.046(1)
C(12B)	−0.3260(3)	0.7785(2)	0.5228(2)	0.051(1)
C(13B)	−0.4294(3)	0.7570(2)	0.4938(2)	0.051(1)
C(14B)	−0.5122(3)	0.7180(2)	0.5394(2)	0.049(1)
C(15B)	−0.5841(3)	0.6538(2)	0.6591(2)	0.050(1)
C(16B)	−0.5722(3)	0.6438(2)	0.7340(2)	0.051(1)
C(17B)	−0.4786(3)	0.6751(2)	0.7692(2)	0.049(1)
C(18B)	−0.3939(3)	0.7192(2)	0.7299(2)	0.048(1)
C(19B)	−0.4016(3)	0.7311(2)	0.6496(2)	0.045(1)
C(20B)	−0.4997(3)	0.7011(2)	0.6159(2)	0.044(1)
C(21B)	−0.1324(6)	0.6475(3)	0.4041(4)	0.098(3)
C(22B)	−0.2130(3)	1.1112(2)	0.4973(2)	0.062(2)
C(23B)	0.1579(3)	0.8398(3)	0.2675(2)	0.072(2)
C(24B)	0.2871(4)	0.8285(4)	0.2833(3)	0.099(2)
C(25B)	0.1519(5)	0.8689(4)	0.1873(2)	0.119(3)
C(26B)	−0.4489(4)	0.7738(4)	0.4125(3)	0.072(2)
C(27B)	−0.3083(3)	0.7533(3)	0.7741(2)	0.072(2)
C(28B)	−0.6763(3)	0.6099(3)	0.6189(2)	0.076(2)
C(29B)	−0.8055(4)	0.6539(6)	0.6508(4)	0.156(4)
C(30B)	−0.6504(7)	0.5084(4)	0.6119(5)	0.211(5)
O(1B)	−0.3135(2)	0.9661(2)	0.5358(2)	0.060(1)
O(2B)	−0.2010(2)	1.1931(2)	0.5076(2)	0.073(1)
O(3B)	−0.0005(2)	1.1497(2)	0.4158(2)	0.057(1)
O(4B)	0.1711(2)	1.0274(2)	0.3108(2)	0.063(1)
O(5B)	−0.2119(2)	0.7851(2)	0.6271(2)	0.059(1)
O(6B)	−0.2973(2)	0.7347(2)	0.8405(2)	0.083(1)
O(7B)	−0.4762(2)	0.6572(2)	0.8428(2)	0.064(1)
O(8B)	−0.6501(2)	0.6007(2)	0.7792(2)	0.070(1)
C(1′)	0.1539(8)	0.4671(6)	0.2844(7)	0.150(4)
C(2′)	0.1348(6)	0.4600(5)	0.3614(8)	0.153(4)
C(3′)	0.1917(9)	0.5105(8)	0.4104(5)	0.174(5)
C(4′)	0.2662(10)	0.5658(6)	0.3819(7)	0.196(6)
C(5′)	0.2852(7)	0.5679(6)	0.3016(8)	0.163(5)
C(6′)	0.2274(9)	0.5200(8)	0.2557(5)	0.158(5)

b. gossypol: chloroform

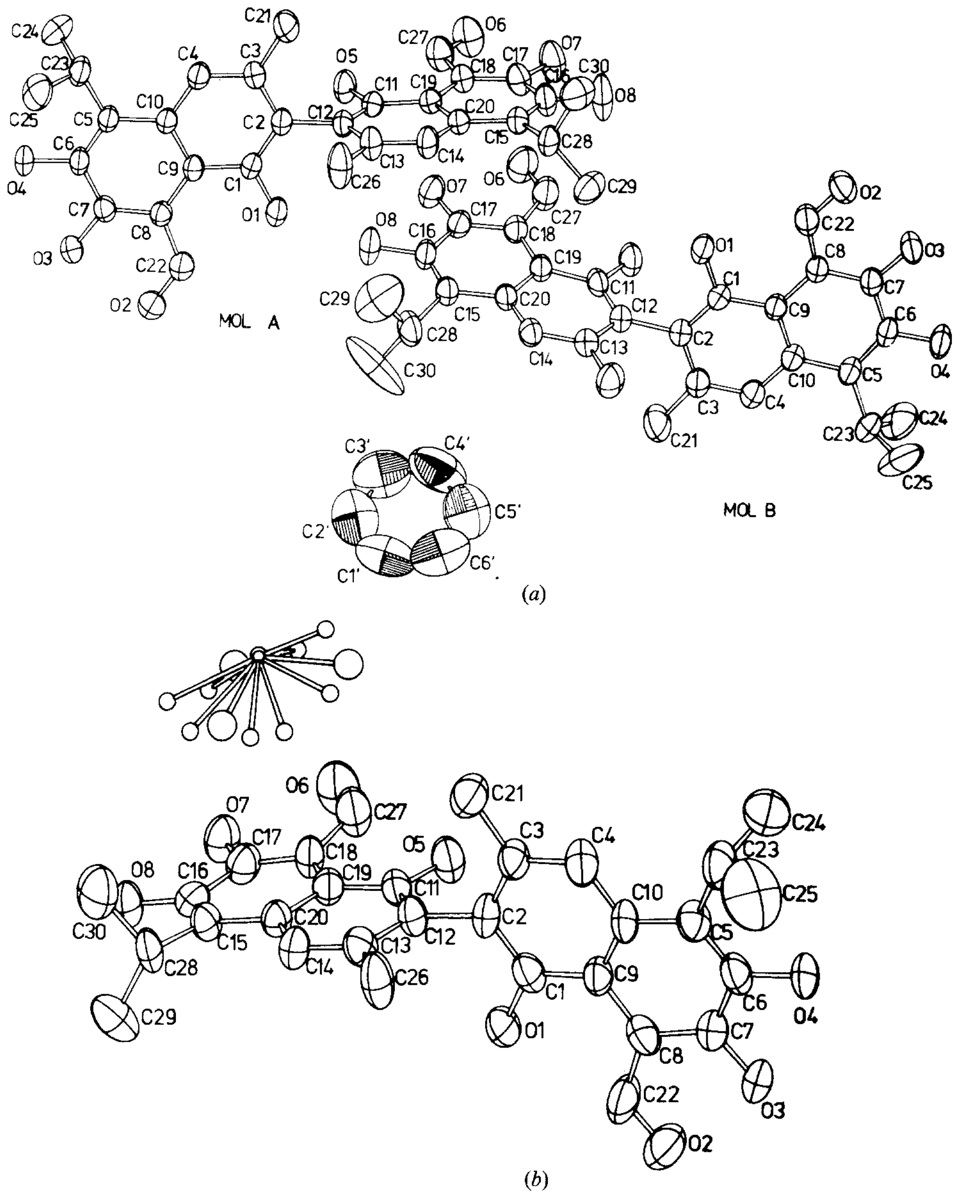
Atom	*x/a*	*y/b*	*z/c*	U_{eq}
C(1)	0.3411(4)	0.053(1)	0.5418(4)	0.061(4)
C(2)	0.3878(3)	0.071(1)	0.5347(4)	0.062(4)
C(3)	0.3895(3)	0.105(1)	0.4837(4)	0.062(4)
C(4)	0.3459(4)	0.113(1)	0.4413(4)	0.073(5)
C(5)	0.2548(4)	0.096(1)	0.4012(4)	0.060(4)
C(6)	0.2099(4)	0.089(1)	0.4091(4)	0.065(5)
C(7)	0.2058(4)	0.061(1)	0.4600(4)	0.064(4)
C(8)	0.2480(4)	0.038(1)	0.5046(4)	0.069(4)
C(9)	0.2968(3)	0.057(1)	0.4977(4)	0.055(4)
C(10)	0.2987(4)	0.086(1)	0.4470(4)	0.059(4)
C(21)	0.4394(4)	0.134(2)	0.4761(4)	0.096(5)
C(22)	0.2390(4)	−0.004(2)	0.5531(5)	0.126(8)

Table I. (continued)

Atom	x/a	y/b	z/c	U_{eq}
C(23)	0.2578(4)	0.109(2)	0.3447(4)	0.085(6)
C(24)	0.2448(5)	0.264(2)	0.3216(5)	0.123(8)
C(25)	0.2290(6)	−0.011(2)	0.3068(6)	0.016(1)
O(1)	0.3388(2)	0.0237(8)	0.5916(3)	0.078(3)
O(2)	0.1966(3)	−0.015(1)	0.5562(3)	0.130(5)
O(3)	0.1599(3)	0.0511(8)	0.4633(3)	0.084(3)
O(4)	0.1658(2)	0.1039(8)	0.3674(3)	0.080(3)
C(11)	0.4529(3)	0.182(1)	0.6118(4)	0.052(4)
C(12)	0.4342(3)	0.057(1)	0.5822(4)	0.055(4)
C(13)	0.4577(4)	−0.083(1)	0.5969(4)	0.061(4)
C(14)	0.4988(3)	−0.091(1)	0.6415(4)	0.061(4)
C(15)	0.5625(3)	0.023(1)	0.7201(4)	0.053(4)
C(16)	0.5780(3)	0.143(1)	0.7513(4)	0.060(4)
C(17)	0.5567(4)	0.289(1)	0.7349(4)	0.063(5)
C(18)	0.5173(3)	0.307(1)	0.6891(4)	0.059(4)
C(19	0.4965(3)	0.178(1)	0.6574(4)	0.055(4)
C(20)	0.5191(3)	0.038(1)	0.6730(4)	0.049(4)
C(26)	0.4366(4)	−0.223(1)	0.5661(5)	0.091(5)
C(27)	0.5037(4)	0.459(2)	0.6732(5)	0.085(5)
C(28)	0.5900(4)	−0.123(1)	0.7349(4)	0.063(4)
C(29)	0.5889(5)	−0.190(1)	0.7894(4)	0.094(5)
C(30)	0.6437(4)	−0.109(2)	0.7324(5)	0.109(7)
O(5)	0.4289(3)	0.3151(7)	0.5970(3)	0.075(3)
O(6)	0.5207(3)	0.5695(8)	0.7014(3)	0.099(4)
O(7)	0.5779(2)	0.4028(7)	0.7677(3)	0.074(3)
O(8)	0.6171(2)	0.1411(7)	0.7992(3)	0.068(3)
CL(1A)	0.3699(7)	0.487(2)	0.3370(6)	*0.188(9)
CL(2A)	0.4411(5)	0.551(2)	0.4382(5)	*0.189(7)
CL(3A)	0.3801(7)	0.784(2)	0.3778(9)	*0.23(1)
CL(1B)	0.3377(8)	0.670(4)	0.3207(9)	*0.20(1)
CL(2B)	0.4222(10)	0.756(4)	0.4078(11)	*0.16(1)
CL(3B)	0.4048(12)	0.448(3)	0.3809(16)	*0.22(2)
CL(1C)	0.3821(8)	0.444(2)	0.3476(8)	*0.085(5)
CL(2C)	0.3620(10)	0.756(2)	0.3419(11)	*0.155(8)
CL(3C)	0.4389(8)	0.636(4)	0.4306(8)	*0.16(1)
CL(1D)	0.3611(11)	0.564(3)	0.3247(8)	*0.16(1)
CL(2D)	0.4023(13)	0.805(2)	0.3953(10)	*0.14(1)
CL(3D)	0.4147(11)	0.506(3)	0.4343(10)	*0.19(1)
C(31)	0.3810(4)	0.595(2)	0.3951(5)	*0.164(6)

*isotropic temperature factor

and *S*, of gossypol exist. The sample of gossypol used for our studies was racemic. The two napthyl moieties of the gossypol molecule are nearly perpendicular, the dihedral angles between their least-squares planes being 88.2(1), 79.1(1) and 89.5(2)° in molecules A and B of GPBNZ and in GPCLF, respectively. There are four intramolecular hydrogen bonds in the gossypol molecule. The geometry of these bonds in GPBNZ is given in Table II.



(*a*)

(*b*)

Fig. 1. ORTEP [10] drawing (50% probability level) and the atom numbering scheme of the gossypol and guest molecules in (a) GPBNZ; (b) GPCLF.

3.2. CRYSTAL STRUCTURE

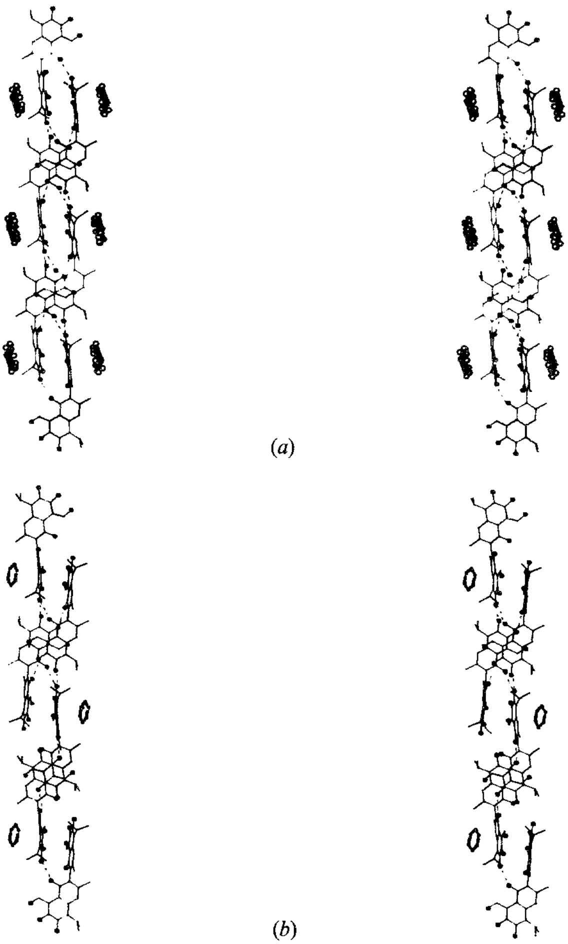
In many lattice inclusion complexes of gossypol the host lattice is constructed from centrosymmetric dimers of gossypol *via* a pair of hydrogen bonds O(5)—H···O(3). These dimers can be the only associates of the host molecules in the structure [11], but in many cases they are further connected by hydrogen bonds to form columns [3, 5, 16] or bilayers [12–15] of the host molecules.

Table II. Geometry of hydrogen bonds in GPBNZ

D—H...A	D...A (Å)	D—H (Å)	H...A (Å)	D—H...A (°)
(a) intramolecular hydrogen bonds				
O(3A)—H(30A)...O(2A)	2.435(3)	0.94(4)	1.57(4)	152(4)
O(7A)—H(70A)...O(6A)	2.491(4)	1.03(5)	1.57(5)	146(4)
O(3B)—H(30B)...O(2B)	2.458(3)	0.96(3)	1.59(3)	150(3)
O(7B)—H(70B)...O(6B)	2.471(3)	1.06(4)	1.53(4)	145(3)
O(4A)—H(40A)...O(3A)	2.632(3)	0.90(4)	2.08(4)	119(3)
O(8A)—H(80A)...O(7A)	2.593(4)	1.09(6)	2.00(6)	111(4)
O(4B)—H(40B)...O(3B)	2.660(3)	1.07(5)	2.08(4)	111(3)
O(8B)—H(80B)...O(7B)	2.593(3)	0.90(5)	2.03(5)	119(4)
(b) intermolecular hydrogen bonds				
O(5A)—H(50A)...O(3A^{i})	2.751(3)	0.96(4)	2.00(4)	134(3)
O(5B)—H(50B)...O(3B^{ii})	2.748(3)	1.06(4)	1.91(3)	133(4)
O(4A)—H(40A)...O(5A^{i})	3.195(3)	0.90(4)	2.39(4)	149(3)
O(4B)—H(40B)...O(5B^{ii})	2.985(3)	1.07(5)	1.96(4)	158(4)
O(1A)—H(10A)...O(8B^{iii})	2.766(3)	0.85(4)	2.17(3)	127(3)
O(8B)—H(80B)...O(4A^{iv})	3.170(3)	0.90(5)	2.46(4)	136(4)

Symmetry codes:
(i) $-x, 1-y, -z$
(ii) $-x, 2-y, 1-z$
(iii) $-1-x, 1-y, 1-z$
(iv) $-1+x, y, 1+z$

The structure of GPCLF is isostructural with the gossypol : iso-valeric acid inclusion complex. As has already been reported [5], in this type of lattice inclusion complexes there are centrosymmetric dimers *via* a pair of O(5)—H···O(3) hydrogen bonds. The dimers, which are related by a two-fold axis, are connected further *via* pairs of hydrogen bonds O(1)—H···O(8) and O(8)—H···O(4) and form a column of host molecules parallel to the [1 0 1] direction (Figures 2a, 3). The planes of the naphthyl moieties C(1)—C(10) and C(11—C(20) are parallel to the axis of the column and the two naphthyl nuclei C(11)—C(20) which are related by the 2-fold axis form a dihedral angle of 19.3(2)°. The hydrophilic groups of the gossypol molecules are hidden in the interior of the column and therefore there are no hydrogen bond interactions between neighbouring columns. Columns which are related by translation along the *b* axis pack parallel and form layers of host molecules. These layers are separated by layers of guest molecules giving an intercalate-type structure of the inclusion compound (Figure 3). Very shallow, hydrophobic depressions are located on the two sides of the column oriented towards the interlayer spaces. The floor consists of the C(11)—C(20) naphthyl ring. As mentioned in the experimental section, the chloroform molecule shows an appreciable disorder. It is disordered in the crystal around the C(31)—H bond. The mean plane calculated through the chloroform Cl atoms is nearly parallel [4.6(4)°] and at a distance of 4.1 Å from the C(11)—C(20) ring located in the depression of the column. The C—H bond of the chloroform molecule is oriented towards the


(a)

(b)

Fig. 2. Columns of the host molecules: (a) GPCLF structure, (b) GPBNZ structure.

other layer of the host and a hydrogen bond between the chloroform C(31) and aldehyde O(2) atoms [C(31)···O(2) 2.98 Å] is formed.

In GPBNZ two types of centrosymmetric dimers formed *via* the O(5)—H···O(3) hydrogen bond can be distinguished: dimers of molecules A related by the symmetry center at (0 1/2 0) and dimers of molecules B related by the symmetry center at (0 0 1/2). These dimers are joined by the hydrogen bonds O(1A)—H···O(8B) and O(8B)—H···O(4A) forming a column of host molecules parallel to the [2 1 $\bar{1}$] direction (Figures 2b, 4). The geometry of the hydrogen bonds is given in Table II. The hydrophilic groups of the host are located inside the column and therefore there are no hydrogen bond interactions between neighbouring columns. As one can easily notice from Figure 2, even though the columns of gossypol molecules look similar in GPBNZ and GPCLF, there are two hydrogen bonds, O(8)A—H···O(4B) and O(1B)—H···O(8A), missing in GPBNZ because the contacts O(8A)···O(4B) and O(1B)···O(8A) are increased to 3.519(4) Å and

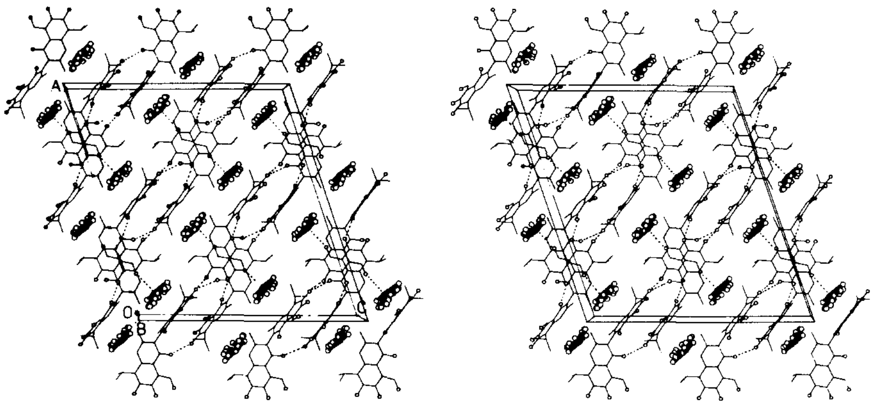


Fig. 3. Stereoview of the crystal packing [PLUTO (9)] of GPCLF.

4.448(4) Å, respectively. The hydroxyl group O(1B)—H is not involved in any hydrogen bonding but, instead, gives a close contact along the column with the methyl group C(29) of molecule A. Columns of the host when compared with the GPCLF structure show the deepening of one depression on the column and the removal of the other. The number of depressions is reduced to one half of those in GPCLF and the host : guest molecule ratio is changed from 1 : 1 in GPCLF to 2 : 1 in GPBNZ. The columns of the host molecules which are related by translation along the *a* axis form a layer which has on its surface V-shaped depressions (Figure 4). The depression is formed by the naphthyl rings C(11)—C(20) of molecule B and C(1)—C(10) of molecule A from the adjacent columns in the layer. Those rings form a dihedral angle of 75.7(2)°. The benzene molecule which is located in this cavity shows a moderate thermal motion and forms angles of 20.1(2)° and 58.2(2)° with the C(11B)—C(20B) and C(1A)—C(10A) rings, respectively. The guest molecule is enclosed in this cavity by the parallel layer of host molecules and a clathrate-type inclusion complex is formed.

The schematic packing of the centrosymmetric gossypol dimers and the guest molecules in the GPBNZ- and GPCLF-type structures is shown in Figure 5. If

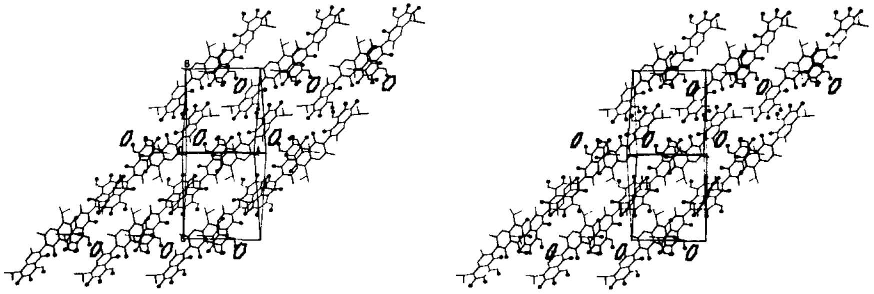


Fig. 4. Stereoview down [0 1 1] of the layer formed by the columns of the host molecules along the *a* axis in GPBNZ.

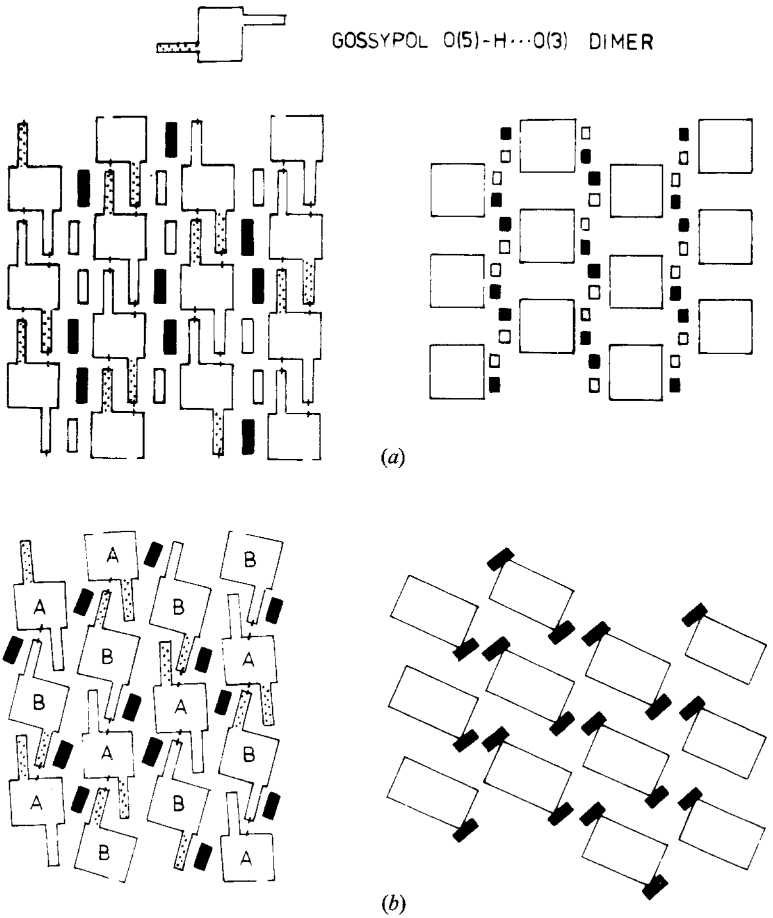


Fig. 5. Schematic comparison of the GPCLF- and GPBNZ-type structures.

every second pair of the guest molecules related by a 2-fold screw axis (white rectangles, Figure 5a) is removed, which results in the gossypol dimers in the host columns being slightly rearranged to fill in the empty space, the crystal symmetry is lowered from $C2/c$ to $P\bar{1}$. In consequence, the host : guest ratio is changed from 1 : 1 to 2 : 1 and a structure of the GPBNZ-type is formed (Figure 5b). On the basis of comparision of the crystal packing of GPCLF and GPBNZ one can postulate that in the desorption process of the intercalate-type GPCLF complex an intermediate clathrate structure of the GPBNZ-type should be formed.

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