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B R I E F C O M M U N I C A T I O N S

X-RAY STRUCTURE ANALYSIS OF GOSSYPOL AND ITS DERIVATIVES. XXX. STRUCTURE OF THE COMPLEX OF BIS-N,N′-DIMETHYLAMINOETHYLIMINOGOSSYPOL AND ACETONE

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Gossypol is a physiologically active pigment that is isolated from cotton and can exist in three tautomeric forms as an aldehyde, lactol, and quinoid [1]. Studies of IR, electronic, and PMR spectra of several alkyl- and arylamines of gossypol in various solutions showed [2] that the tautomeric form depends on the nature of the amine. The primary form for alkylimines is the quinoid form; for arylamines, benzoid. It is known that dianilinegossypol and di-α-(-)-phenylethylaminegossypol exist in the crystals as the quinoid tautomer [3, 4]. An x-ray structure analysis of bis-N,N′-dimethylaminoethyliminegossypol (**1**), which was synthesized from gossypol [5], was carried out in order to explain the tautomerism of gossypol alkylimines and the characteristics of their crystal packing.

Single crystals were grown from acetone solution at room temperature. The crystallographic parameters were determined on a automated four-circle Syntex-$P2_1$ diffractometer: space group $P1^{-}$, a = 11.320(2) Å, b = 11.493(2) Å, c = 16.973(2) Å, α = 94.75(2)°, β = 108.44(2)°, γ = 102.67(2)°, V = 2016.0(7) Å^3, Z = 2, D_{calc} = 1.178 g/cm^3. Integrated intensities were measured by $\theta/2\theta$-scanning ($2.8 < \theta < 62.9°$) using Cu Kα-radiation. The total number of reflections was 3190. After applying Lorentz and polarization corrections and removing reflections with $I < 2\sigma(I)$, the data set consisted of 2958 reflections. The structure was solved by direct methods using the SHELXS programs [6] and refined using the SHELXL-97 programs [7]. H atoms (with the exclusion of active ones involved in H-bonds) were fixed geometrically and refined using the rider model. The agreement factor R = 0.053. The structure was deposited under number CCDC 235924.

Figure 1 shows the conformation of **1** and the atomic numbering. The molecule consists of two identical fragments bonded by a single bond (C2–C12). The naphthalene fragments C1-C10 and C11-C20 are planar (within 0.014 and 0.018 Å, respectively). The dihedral angle between them is 101.3°. The dimethylaminoethylimine fragment in one half of **1** is disordered at two positions with packing coefficients of 0.63 and 0.37, respectively.

The molecular structure of **1** includes two intramolecular H-bonds. H-bond N–H...O=C closes a six-membered ring containing O3-C7-C8-C22-N1-HN1 (O7-C17-C18-C27-N2-HN2). H-bonds of the O–H...O type close five-membered rings consisting of O3-C7-C6-O4-HO4 (O7-C17-C16-O8-HO8). An analysis of the geometry of the bond distances and the unambiguous appearance in different syntheses of H atoms on N1 and N2 indicate that bis-N,N′-dimethylaminoethyliminegossypol in its solvate crystals exists as the quinoid tautomer.

Host—guest pairs form in crystals of **1** and acetone through an O1–H...O1S H-bond [2.809(9) Å, 124(6)°]. Molecules of **1** themselves are joined into centrosymmetric dimers through O5–H...O3 H-bonds [2.696(5) Å, 136(4)°]. The naphthalene fragments of the two molecules in these dimers are coplanar to each other (0.1°) and separated by a distance of 3.36 Å. This is typical of π—π (stacking) interactions and additionally stabilizes the dimer. The dimers are arranged into columns parallel to the [101^{-}] direction through a centrosymmetric pair of H-bonds O8–H..O7 [2.764(5) Å, 132(5)°] (Fig. 2).

Thus, the x-ray structure analysis established that both arylamines and alkylamines of gossypol are found in crystals as the quinoid tautomer.

The structure was registered in the Cambridge Structural Database under number CCDC 235924.

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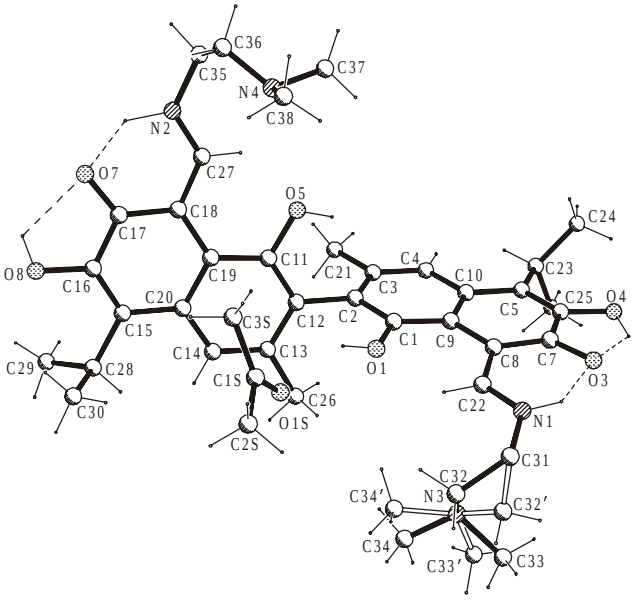

Fig. 1

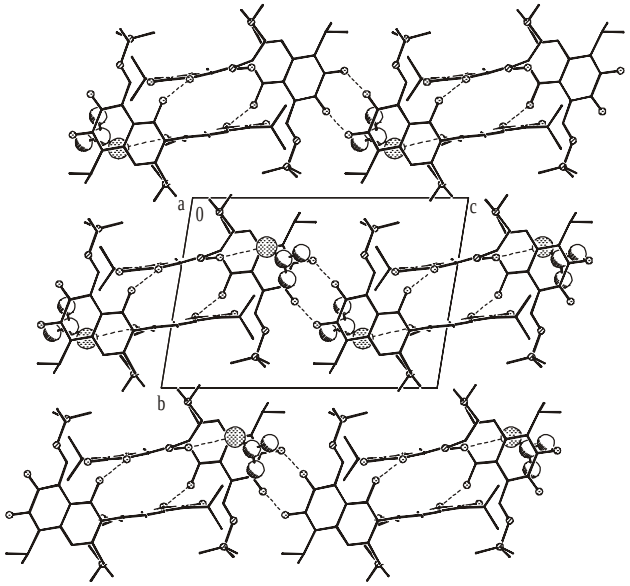

Fig. 2

Fig. 1. Conformation of the complex of **1** and acetone and atomic numbering. Dashed lines show intramolecular H-bonds.
Fig. 2. Crystal structure of the complex of **1** and acetone projected on the (0yz) plane. Dashed lines show intermolecular H-bonds.

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