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A Study on the Crystal Structure of a Solid Solution of Monoazoacetoacetanilide Yellow Pigments

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ABSTRACT

A single crystal of the solid solution containing 40% mol CI Pigment Yellow 1 and 60% mol CI Pigment Yellow 5 was obtained and its crystal structure determined by single crystal X-ray diffraction techniques. It crystallizes in the monoclinic system with the cell parameters $a = 7{\cdot}581(5)$ Å, $b = 20{\cdot}379(2)$ Å, $c = 10{\cdot}406(2)$ Å, $\beta = 98{\cdot}30(3)^\circ$, *the space group is* $P2_1/n$ *and there are four molecules per unit cell. There are intramolecular hydrogen bonds which tend to keep the molecule planar and the adjacent molecules are linked by Van der Waals forces. The results indicate that the molecules of CI Pigment Yellow 5 are introduced into the lattice of CI Pigment Yellow 1 and replace some molecules of it at random to form a solid solution with the crystal packing of CI Pigment Yellow 1 as a worthy crystal packing, although the amount of CI Pigment Yellow 1 is 20% less than that of CI Pigment Yellow 5. Some crystal structures of related pigments have been compared; it is also concluded that the solid solution is isomorphous with CI Pigment Yellow 1 and Hansa Yellow 6G.*

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1 INTRODUCTION

It is recognized that the colour of organic colorants is mainly determined by the electronic interactions within the molecular system which composes the dyes. Unlike dyes, pigments are used in the solid state and the absorption characteristics of the chromophore can be significantly influenced and modified by the electronic interactions of the close-packed molecules. Thus the colour properties of pigments depend not only on the molecular constitution but also on their crystallographic arrangement. Therefore the full colour parameters and colour–constitution relationships of pigments must be based on two factors, viz. the absorption properties determined by the chromophores, which can be investigated using PPP-MO methods;[1] and also the effect of close-packed chromophores, e.g. their crystal structure. An investigation has been reported to correlate the molecular crystal packing and the colour properties of a series of perylene-3,4:9,10-bis(dicarboximide) pigments.[2]

In some applications, mixtures of pigments which are purposely synthesized together to obtain favourable colouring properties, are defined as synergistic pigments. In previous studies, synergistic relations between several mixed synthetic pigments have been found, the results showed that a solid solution was formed between the two pigments, thus leading to improvements in the colour properties of the pigments.[3]

In this present paper, attempts are made to study the crystal structure of the solid solution of CI Pigment Yellow 5 in CI Pigment Yellow 1.

2 EXPERIMENTAL

Single crystals were obtained from experimentally mixed pigments containing 40% CI Pigment Yellow 1 and 60% CI Pigment Yellow 5 by slow cooling of a saturated toluene solution from 85°C to room temperature. Optical extinction showed the existence of yellow blade-like crystals with oblique extinction on the blade face.

The crystal chosen for intensity measurements was of approximate size $0{\cdot}13 \times 0{\cdot}2 \times 0{\cdot}27$ mm. An ENRAT-NONIUS CAD-4 diffractometer equipped with computer Micro VA II with programs of the SDP-PLUS Package was used for the determination of the cell constants and the crystal structure.

The cell parameters were calculated and refined from the setting angles of 25 reflections with θ ranging from 9° to 12°; the crystal data obtained were as follows: $a = 7{\cdot}581(3)$, $b = 20{\cdot}379(3)$, $c = 10{\cdot}406(3)$ Å, $\beta = 98{\cdot}30(3)°$, $Z = 4$, $V = 1513{\cdot}6$ Å,^{3} $D_{\mathrm{cal}} = 1{\cdot}362$ g/cm^3.

The integrated intensities of the reflections with $\theta < 25°$ were collected using a 2θ–2θ scan mode and graphite-monochromated Mo, K_α radiation. The scan width was $0{\cdot}9 + 0{\cdot}34 \tan\theta$ and the aperture $2{\cdot}70 + 1{\cdot}05 \tan\theta$ in mm. Three reflections were used for intensity and orientation control. A total of 2888 reflections were measured, of which 1020 with $I > 3\sigma(I)$ were considered and used for the refinements after corrections for lorentz, polarization, empirical and absorption effects. Transmission factors varied from 93·28% to 99·98%. The scattering factors for C, O, N, H atoms were taken from the *International Tables for X-ray Crystallography.*[4]

The structure was resolved by direct methods and developed by the difference Fourier synthesis. The hydrogen atoms were located by a difference electron density map and geometry calculation and were not

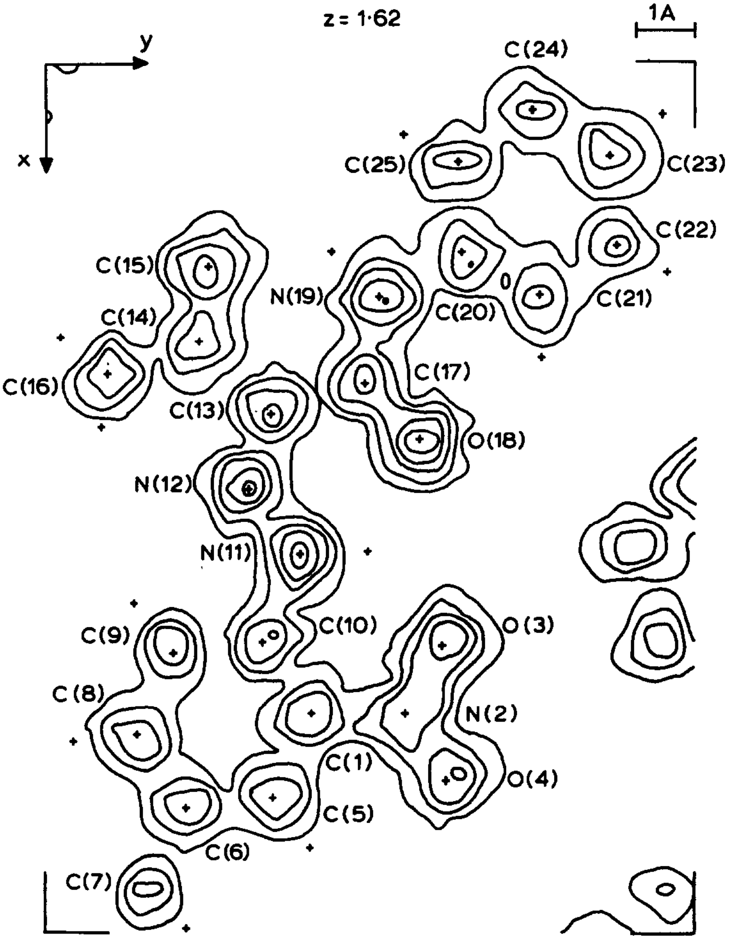


Fig. 1. A composite electron density map of the molecule; the molecule is projected down the a-axis. The contour is at intervals of $1{\cdot}62\,\mathrm{e}/\text{Å}^3$

further refined. The unit weighting scheme, ω, was used as follows:

$$\omega = 1 \quad \text{when the reflection } I > 3\sigma(I)$$
$$\omega = 0 \quad \text{when the reflection } I \leqslant 3\sigma(I)$$

The refinement by full matrix least squares for scale factor, coordinates, anisotropic temperature factors of the non-hydrogen atoms converged at the final $R_1 = 0{\cdot}0439$, $R_2 = 0{\cdot}0443$ (where $R_1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$, $R = [\Sigma\omega|F_o^2 - F_c^2|/\Sigma\,\omega F_o^2]^{1/2}$.) The final atomic parameters are listed in Table 1 and a composite electron density map is given in Fig. 1. The proposed molecular structure is shown in Fig. 2.

TABLE 1
The Atomic Positional Parameters and Their Estimated Standard Deviations

Atom	*x*	*y*	*z*	*B(A)*
C(1)	0·4875(8)	0·0295(3)	0·2523(5)	3·61(1)
N(2)	0·5114(7)	−0·0410(3)	0·2663(5)	4·6(1)
O(3)	0·4385(7)	−0·0776(2)	0·1817(4)	6·1(1)
O(4)	0·6369(7)	−0·0620(3)	0·3613(5)	7·0(1)
C(5)	0·5686(8)	0·0687(3)	0·3540(6)	4·3(1)
C(6)	0·5526(9)	0·1363(3)	0·3508(6)	4·5(2)
C(7)	0·632(1)	0·1791(4)	0·4590(8)	2·7(2)
C(8)	0·4575(9)	0·1632(3)	0·2392(6)	4·7(2)
C(9)	0·3749(8)	0·1257(3)	0·1383(6)	4·2(2)
C(10)	0·3855(7)	0·0571(3)	0·1433(5)	3·4(1)
N(11)	0·2946(7)	0·0194(2)	0·0417(4)	3·4(1)
N(12)	0·1917(6)	0·0509(2)	−0·0517(4)	3·5(1)
C(13)	0·1000(8)	0·0194(3)	−0·1479(5)	3·3(1)
C(14)	−0·0078(8)	0·0640(3)	−0·2420(6)	3·9(1)
O(15)	−0·0973(6)	0·0434(2)	−0·3402(4)	5·6(1)
C(16)	−0·002(1)	0·1363(3)	−0·2127(7)	5·4(2)
C(17)	0·1006(7)	−0·0534(3)	−0·1599(5)	3·3(1)
O(18)	0·1821(6)	−0·0877(2)	−0·0748(4)	4·2(1)
N(19)	0·0047(6)	−0·0768(2)	−0·2706(4)	3·6(1)
C(20)	−0·0213(8)	−0·1432(3)	−0·3113(5)	3·4(1)
C(21)	0·0277(9)	−0·1972(3)	−0·2334(6)	4·3(1)
C(22)	−0·0081(9)	−0·2594(3)	−0·2846(6)	4·7(2)
C(23)	−0·0911(9)	−0·2685(3)	−0·4105(6)	4·9(2)
C(24)	−0·1405(9)	−0·2143(3)	−0·4857(6)	5·0(2)
C(25)	−0·1052(8)	−0·1517(3)	−0·4383(6)	4·4(2)
H(71)	0·707	0·217	0·443	3·5*
H(72)	0·543	0·196	0·498	3·5*
H(73)	0·702	0·152	0·521	3·5*
H(11)	0·293	−0·035	0·057	4·3*
H(161)	−0·043	0·166	−0·279	6·7*
H(162)	−0·073	0·146	−0·143	6·7*
H(163)	0·118	0·150	−0·179	6·7*
H(19)	−0·082	−0·049	−0·332	4·8*

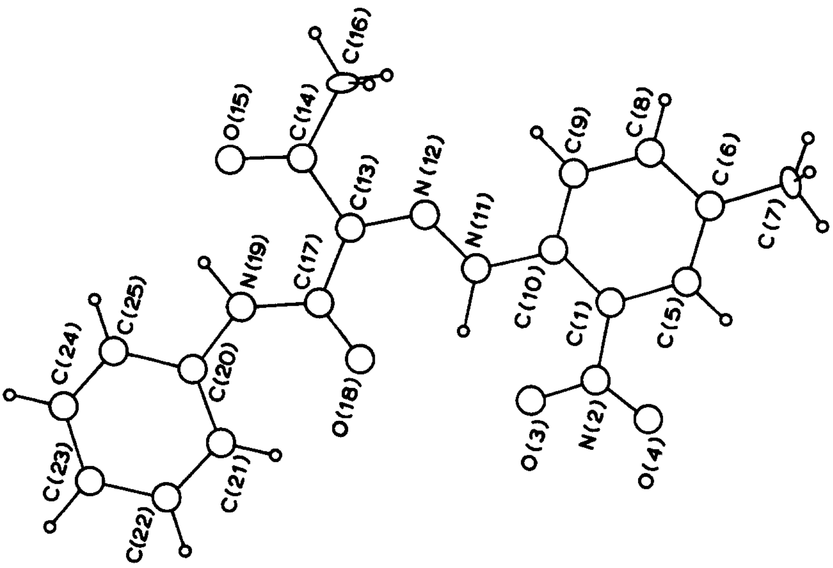


Fig. 2. Proposed molecular structure projected on the plane containing atoms N(11), N(12), C(13) and the phenyl ring adjacent to the hydrazone form.

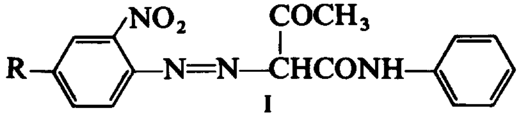
Starred atoms in Table 1 were refined isotropically; anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$4/3 * [a * B(1,1) + b * B(2,2) + c * B(3,3) + ab * \cos * B(1,2) + ac * \cos * \beta(1,3) + bc * \cos * B(2,3)]$$

3 RESULTS AND DISCUSSION

3.1 Molecular structure and tautomerism

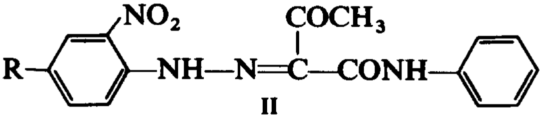
It is well known that there are two tautomers, these being the most likely to exist in the solid state of the monoazoacetoacetanilide yellow pigments. I is the azo tautomer and II is the hydrazone form.



$R{-}C_6H_3(NO_2){-}N{=}N{-}CH(COCH_3)CONH{-}C_6H_5$

I

When R = CH_3
When R = H



$R{-}C_6H_3(NO_2){-}NH{-}N{=}C(COCH_3){-}CONH{-}C_6H_5$

II

CI Pigment Yellow 1
CI Pigment Yellow 5

The two formulae show that the two structures differ as to whether certain of the N(11)–N(12) bonds are single or double or the hydrogen atom is linked to C(13) or N(11) and that the bond length would be different depending upon whether they are single or double.

Tables 2 and 3 list the bond lengths and angles respectively. Comparison with the accepted bond lengths (Table 4), indicated that N(12)–C(13) formed a double bond but its value (1·302 Å) is shorter than that of the accepted value (1·32 Å). The N(11)–N(12) bond has some delocalizations, as its value is between the accepted values of single and double bonds. The results indicate that the hydrazone form is the best proposed structure.

Further evidence to support structure II is obtained as the H atoms positions are determined by a difference Fourier synthesis. The determination shows that there is a hydrogen atom bonded to N(11), but there is no sign of this to C(13). The fact gives direct evidence confirming that the azo bond does not exist, otherwise a hydrazone form would exist in the solid state of the monoazoacetoacetanilide yellow pigments. This agrees with previous structure determinations of Whitaker.[5]

3.2 Intramolecular hydrogen bonds and planarity of the molecule

The interatomic distances were calculated during the determination of the structure. The most noticeable are as follows:

Nitrogen N(11)–Oxygen O(3) = 2·5996 + 0·0063 Å
Nitrogen N(11)–Oxygen O(18) = 2·5803 + 0·0061 Å
Nitrogen N(11)–Oxygen O(15) = 2·6400 + 0·0069 Å

These suggest that there is a bifurcated hydrogen bond from N(11) and a hydrogen bond from N(19). These intramolecular hydrogen bonds will tend to keep the molecule planar.

With regard to the intermolecular hydrogen bonds between columns of molecules (see Table 5), as the distances of the atoms oxygen, nitrogen and carbon are larger than 3·28 Å (which is the limit distance between carbon and oxygen atoms for the formation of hydrogen bonds), then there are no such bonds between the adjacent molecules.

The molecules are not exactly planar, although there are intramolecular hydrogen bonds which tend to keep some parts of the molecule planar. In order to examine the planarity of the molecule, the angles of inclination of the two phenyl groups to the molecules are considered; the equations of three planes (excluding hydrogen atoms) by least squares fit are:

Plane No. 1 $0{\cdot}8979x + 0{\cdot}0471y - 0{\cdot}4376z - 1{\cdot}8577 = 0$
phenyl groups adjacent to hydrazone linkage included

TABLE 2
Bond Lengths (Å)

C(1)–C(2)[a]	1·453(8)	C(1)–C(5)	1·395(9)
C(1)–C(10)	1·397(8)	N(2)–O(3)	1·224(6)
N(2)–O(4)	1·216(7)	C(5)–C(6)	1·385(9)
C(6)–C(7)	1·481(9)	C(6)–C(8)	1·388(9)
C(8)–C(9)	1·374(8)	C(9)–C(10)	1·400(9)
C(10)–N(11)	1·404(7)	N(11)–N(12)	1·321(6)
N(11)–H(11)	1·122(4)	N(12–C(13	1·303(7)
C(13)–C(14)	1·492(8)	C(13)–C(17)	1·488(8)
C(14)–O(15)	1·218(7)	C(14)–C(16)	1·504(9)
C(16)–H(161)	0·939(7)	C(16)–H(162)	0·981(8)
C(16)–H(163)	0·964(7)	C(17)–O(18)	1·223(6)
C(17)–N(19)	1·357(7)	N(19)–C(20)	1·423(9)
N(19)–H(19)	1·023(4)	C(20–C(21)	1·385(8)
C(20)–C(25)	1·393(7)	C(21)–C(22)	1·388(8)
C(22)–C(23)	1·382(8)	C(23)–C(24)	1·373(8)
C(24)–C(25)	1·382(8)	C(7)–H(71)	0·985(9)
C(7)–H(71)	0·959(9)	C(7)–H(73)	0·955(8)

[a] Numbers in parentheses are estimated deviations in the least significant digits.

TABLE 3
Bonding Angles (Interatomic Angles) (Degrees)

N(2)–C(1)–C(5)	117·0(6)	N(2)–C(1)–C(10)	121·8(5)
C(5)–C(1)–C(10)	121·2(6)	C(1)–N(2)–O(3)	119·6(5)
C(1)–N(2)–O(4)	118·7(6)	O(3)–N(2)–O(4)	121.8(7)
C(1)–C(5)–C(6)	121·7(7)	C(5)–C(6)–C(7)	122·9(8)
C(5)–C(6)–C(8)	116·5(6)	C(7)–C(6)–C(8)	120·6(7)
C(6)–C(8)–C(9)	123·0(6)	C(8)–C(9)–C(10)	120·6(6)
C(1)–C(10–C(9)	117·0(6)	C(1)–C(10)–N(11)	123·0(5)
C(9)–C(10)–N(11)	120·0(6)	C(10)–N(11)–N(12)	117·4(4)
C(10–N(11)–H(11)	116·9(5)	N(12)–N(11)–H(11)	124·4(5)
N(11)–N(12)–C(13)	121·2(5)	N(12–C(13)–C(14)	112·6(5)
N(12)–C(13)–C(17)	123·2(5)	C(14)–C(13)–C(17)	124·1(6)
C(13)–C(14)–C(16)	117·8(6)	O(15–C(14)–C(16)	120·3(6)
C(13)–C(17)–O(18)	121·1(5)	C(13)–C(17)–N(19)	114·5(5)
O(18)–C(17)–N(19)	142·5(6)	C(17)–N(19)–C(20)	128·5(5)
N(19)–C(20–C(21)	124·5(5)	N(19)–C(20)–C(25)	115·2(5)
C(21–C(20)–C(25)	120·3(6)	C(20–C(21)–C(22)	118·8(5)
C(21)–C(22)–C(23)	121·6(6)	C(22)–C(23)–C(24)	118·9(7)
C(23)–C(24)–C(25)	121·2(5)	C(20)–C(25)–C(24)	119·4(6)

TABLE 4
Accepted Values of Single and Double Bond Lengths[4]

	Bond length (Å)			
	C–O	*N–N*	*N–C*	*C–C*
Single bond	1·43	1·44	1·47	1·54
Double bond	1·23	1·24	1·32	1·34

Plane No. 2 $0{\cdot}9464x - 0{\cdot}0133y - 0{\cdot}3228z - 1{\cdot}3629 = 0$
the other phenyl groups included

Plane No. 3 $1{\cdot}8827x + 0{\cdot}0130y - 0{\cdot}4698z - 1{\cdot}6531 = 0$
phenyl groups (to hydrazone) and the linkage as well as C(20), C(21), C(22) included.

The dihedral angles between the planes are

Plane 1 and Plane 2	7·94 + 0·80°
Plane 1 and Plane 3	2·83 + 1·85°
Plane 2 and Plane 3	9·31 + 0·56°

These results suggest that the phenyl group linked to the hydrazone group is approximately parallel to the molecules as the dihedral angle is less than 3°, but the other phenyl ring is twisted at an angle and make itself inclined to the plane of the molecule. It is clear that the hydrogen bonded form N(11) plays an important role in holding the first phenyl ring parallel to the plane of the molecule.

TABLE 5
Interatomic Distances in the Crystals (Å)

C(1)–C(17)	3·4326	N(2)–N(12)	2·9273
N(2)–C(13)	3·3323	N(2)–O(15)	3·3388
O(3)–N(12)	3·329	O(3)–C(14)	3·4232
O(3)–O(15)	3·3358	O(3)–C(22)[a]	363578
O(3)–C(23)[a]	3·2778	O(4)–C(5)[a]	3·4213
O(4)–C(13)	3·4714	O(4)–C(14)	3·4458
O(4)–C(25)[a]	3·3372	C(5)–C(17)	3·4541
C(5)–N(19)	3·4726	C(9)–C(20)	3·4567
C(10)–N(19)	3·4344	N(11)–N(11)	3·4426
N(11)–C(13)	3·4279	N(11)–C(17)	3·4692
N(12) C(17)	3·3419	N(12)–O(18)	3·3773

[a] Inter-columnar distances, the other distances are within the columns of adjacent molecules.

The deviations of all the atoms from the three planes have also been calculated. All the three average deviations are less than 0·25 Å; this is very small compared with the size of the molecule and so in spite of the torsion of the phenyl ring, the molecule is approximately planar.

As the crystal structure of the solid solution is similar to that of CI Pigment Yellow 1, the results obtained are almost the same as that of CI Pigment Yellow 1[6] and Hansa Yellow 5G.[7]

3.3 The crystal packing of the solid solution

Examination showed that both kinds of molecules exist in the crystal (see Table 1, the isotropic equivalent displacement parameter of C(7)) and lie in columns parallel to the *a*-axis and the adjacent molecules within the column lie anti-parallel. All intermolecular distances below 3·50 Å were calculated, involving hydrogen atoms; Table 5 lists the distances of the non-hydrogen atoms. Some showed that there are Van der waals contacts between atoms of adjacent molecules, but no intermolecular hydrogen bonds appear. These agree with the results of the determination of Hansa Yellow 5G.

In terms of the molecule packing within the crystals, the two kinds of molecules are stacked at random to form a solid solution. Thus in this case the parent lattice is that of CI Pigment Yellow 1, and the molecules of CI Pigment Yellow 5 replace some molecules of CI Pigment Yellow 1. As the two kinds of pigments form a solid solution with a worthy crystal packing of CI Pigment Yellow 1, the cell dimensions approached that of CI Pigment Yellow 1, although the amount of CI Pigment Yellow 1 is 20% less than that of CI Pigment Yellow 5.

As the molecules of CI Pigment Yellow 5 are introduced into the crystal lattice of the molecules of CI Pigment Yellow 1, the interactions of the chromophores would be changed compared with the case of only one kind of molecule, for example CI Pigment Yellow 1 or CI Pigment Yellow 5. Although the crystal structure of the solid solutions are determined macroscopically, it gives no direct information about that. Further investigation must be carried out to correlate the colour properties and the crystal structures.

3.4 Comparison with Hansa Yellow 5G and related pigments

Table 6 lists the cell dimensions of the related pigments. Hansa Yellow 5G was reported as a mixed crystal containing 47% CI Pigment Yellow 5 and 53% CI Pigment Yellow 1. As the amounts of CI Pigment Yellow 1 are increased, this means that more hydrogen atoms in the molecules of CI Pigment Yellow 5 are substituted by methyl groups and in doing so the unit

TABLE 6
Cell Dimensions of the Related Pigments (Å)

	a	*b*	*c*	*β*°
α-CI Pigment Yellow 5	7·593	20·029	10·217	101·87
Hansa Yellow 5G	7·567	20·420	10·345	99·29
The solid solution	7·581(5)	20·379(2)	10·406(2)	98·30(3)
CI Pigment Yellow 1	7·598	20·375	10·440	98·18

cell volume becomes larger compared with that of Hansa Yellow 5G or CI Pigment Yellow 5, to approach the volumes of CI Pigment Yellow 1. Otherwise the cell dimensions will be decreased. In the present study, the volumes of *a* and *c* have slightly increased compared with the results of Hansa Yellow 5G, although the amounts of CI Pigment Yellow 1 are 10% less than that of Hansa Yellow 5G.

It has already been mentioned and examined by X-ray powder diffraction that the solid solution is isomorphous with CI Pigment Yellow 1 and Hansa Yellow 5G as well as α-form of CI Pigment Yellow 5.[3]

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