Four crystal-structures derived from a yellow pyrazolyl azo pigment

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Abstract

The title compound is a pyrazolyl azo pigment which has good light- and heat-stability, but is rather poor in solvent fastness. X-ray structure analysis has been carried out in order to improve its solvent fastness from the structural point of view. Unexpectedly, two kinds of five-coordinate bisazo Na-complexes (Na-containing B-PAT: space group: P-1) as well as one Na-free monoazo compound (M-PAT: space group: C2/c) were isolated as single crystals. $NaNO_2$ used for the preparation of diazo components is found to be responsible for the Na-complex formation, and the Na atom bridges two monoazo moieties in a cis fashion. On the other hand, elimination of the Na atom by hydrochloric acid yields a Na-free bisazo compound of the trans form (Na-free B-PAT: space group: P-1). Na-free B-PAT is characterized by good solvent fastness in addition to the light- and heat-stability of the original title compound.

1. Introduction

Azo pigments are widely used in imaging and printing industries because of their versatile colors, high tinctorial strength as well as their low price [1]. Therefore, the azo compounds are by far the largest group of colorants with respect to number and production volume of currently marketed dyes and pigments. However, the azo pigments are generally inferior in light-, heat- and solvent-fastness to phthalocyanines (blue), peryleneimides (vivid red *via* maroon to black), quinacridones (red and magenta), pyrrolopyrroles (red), although considerable effort has been directed to improve these properties. On this account, the azo pigment has commercial significance mainly in yellow color. Quite recently, some novel azo pigments with light- and heat-stability (but poor solvent-fastness) have recently been reported by Nagata *et al*. which include 2,6-bis[5-amino-3-*tert*-butyl-4-(3-methyl-1,2,4-thiadizol-5-yldiazeneyl)-1*H*-pyrazol-1-yl]-1,3,5-triazin-4(1*H*)-one (B-PAT: Fig. 1) [2]. In our effort to grow its single crystals for X-ray structure analysis, we have isolated three kinds of single crystals (one mono and two bisazo compounds) from the reaction product. This means that the reaction product is not a pure material, but a mixture of mono and bisazo compounds. To our even greater surprise, the bisazo compounds are found to include Na atoms and form five-coordinate Na-complexes in a *cis* fashion (Na-containing B-PAT: Fig. 2 (a)) [3, 4]; whereas the monoazo compound is Na-free (M-PAT: Fig. 2 (b)) [5]. Then, we wondered why the Na atom is included in B-PAT and why the Na-complex crystallizes in a *cis* fashion which is basically less stable than the *trans* form. $NaNO_2$ used for the preparation of diazo components is found to be responsible for the Na-complex formation, and the Na atom bridges by force two monoazo moieties in a *cis* fashion. At this moment, it struck us that elimination of the Na atom can yield a B-PAT of the *trans* form that is more stable and might be less soluble in organic pigments. In fact, we could isolate Na-free B-PAT of the *trans* form by addition of hydrochloric acid. Then, Na-free B-PAT of the *trans* form is found to possess high solvent fastness in addition to the light- and heat-stability of the original title compound.

The present paper reports on the crystal structure of two Na-containing B-PATs of the *cis* form and one Na-free B-PAT of the *trans* form, as well as Na-free M-PAT.

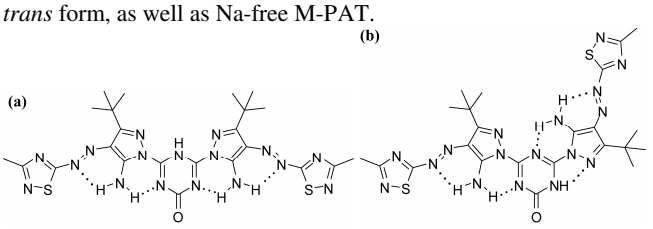

Fig. 1 Structure of B-PAT: (a) cis form and (b) trans form.

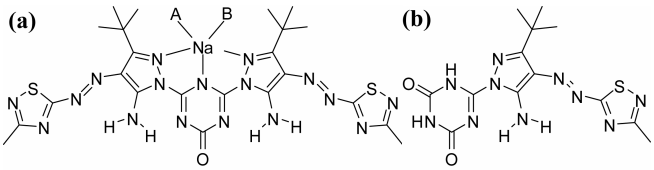

Fig. 2 Structure of three kinds of isolated crystals: (a) Na-containing B-PATs of the cis form (B-PAT I with A = methanol and B = phenol: B-PAT II with A = water and B = NMP) and (b) Na-free M-PAT.

2. Experimental

2.1. Preparation of B-PAT and Na-free B-PAT

The mixture of mono- and bisazo compounds (*i.e.* intended B-PAT: Fig. 1) was synthesized as described in a previous report [2].

Na-free B-PAT was immediately precipitated from a B-PAT-saturated solution in NMP upon dissolution of HCl with 30 times molar equivalent. The product was isolated by filtration and washed with water. Elementary analysis gave the formula of $C_{23}H_{29}N_{17}OS_2 \cdot H_2O$ which is in good agreement with the theoretical value of B-PAT (M_w: $C_{23}H_{29}N_{17}OS_2$ = 623.72) being non-water. In addition, mass spectrum gave the parent peak of 624 for B-PAT together with some small fractions.

2.2. Crystal growth

Single crystals of Na-containing B-PAT I of the *cis* form were grown by recrystallization from a mixed solution of methanol and phenol (1:1 in molar ratio) prepared at 80 °C. Needle shaped crystals were obtained in a closed system saturated with methanol vapor after standing for one week. Similarly, single crystals of Na-

containing B-PAT II of the *cis* form and Na-free M-PAT were obtained from a solution in *N*-methyl-2-pyrrolidone prepared at 100 °C. After standing for one week, single crystals were obtained in the form of needles for both Na-containing B-PAT II and M-PAT. On the other hand, the crystal growth of Na-free B-PAT of the *trans* form was extremely difficult. After many unsuccessful trials, needle-shaped single crystals could only be obtained from chloroform.

2.3. Structure analysis

Since the crystals appeared to include solvents, reflection data were collected at -180 or -120 °C on an R-AXIS RAPID-F diffractometer from Rigaku using Cu$K\alpha$ as the radiation source (λ = 1.5418 Å). In all analyses, the structure was solved by direct methods (SIR2004) [6] and refinement was carried out by the full-matrix least-squares method of F^2 (SHELXL97) [7].

2.4. Molecular orbital calculations

Semi-empirical molecular orbital (MO) calculations were carried out on B-PATs and M-PAT, using MOPAC2009. Geometry was optimized with the AM1 Hamiltonian, and the spectroscopic calculations were made using ZINDO method.

3. Results and discussion

3.1. MO calculations

First of all, we will discuss the stability of the *cis* or *trans* B-PAT molecule, together with that of Na-containing B-PAT. This serves as the basis for discussions of the crystal structure described below.

Table 1 lists the results of the MO calculations, showing the heat of formation and the dipole moments for *cis* B-PAT (Fig. 1(a)), *trans* B-PAT (Fig. 1(b)), Na-containing *cis* B-PAT I (with A = methanol and B = phenol in Fig. 2), and B-PAT II (with A = water and B = NMP). Obviously, the heat of formation of the *trans* form (339.9 kcal/mol) is lower than that of the *cis* form (346.0 kcal/mol) by about 6 kcal/mol, indicating that the *trans* form is more stable than the *cis* one. However, the situation reverses drastically when the Na atom is integrated into *cis* B-PAT (211.3 and 184.0 kcal/mol for Na *cis*-form I and II, respectively). This explains why the Na-containing *cis*-form exists in reality as the most stable structure.

Table 1 MO calculations for four different conformations of B-PAT.

	Heat of formation (kcal/mol)	Dipole momentum (D)
***cis* form**	**346.0**	**2.6**
***trans* form**	**339.9**	**2.3**
Na *cis*-form I	**221.3**	**12.9**
Na *cis*-form II	**184.0**	**16.0**

3.2. Crystal structure

Table 2 details the crystallographic parameters for Na-containing B-PAT I of the *cis* form (with A = methanol and B = phenol in Fig. 2), B-PAT II of the *cis* form (with A = water and B = NMP), Na-free B-PAT of the *trasns* form, and Na-free M-PAT. Among these, only Na-free B-PAT contains no solvents, while all the rest is solvated crystals. M-PAT is characterized by a space group of *C*2/*c*, while the others possess *P*-1. The inclusion of the Na atom comes as a great surprise. $NaNO_2$ used for the preparation of diazo components is found to be responsible for the formation of Na-complexes, and thus the Na atom bridges two monoazo moieties in a *cis* fashion, as described below.

Table 2 Crystallographic parameters.

	Na-containing B-PAT I of the *cis* form	Na-containing B-PAT II of the *cis* form	Na-free B-PAT of the *trans* form	M-PAT
Molecular formula	$C_{30}H_{38}N_{17}O_3S_2Na$ ·4(C_6H_6O)	$C_{28}H_{39}N_{18}O_3S_2Na$ ·C_5H_9NO	$C_{23}H_{29}N_{17}OS_2$	$C_{13}H_{16}N_{10}O_2S$ ·C_5H_9NO·H_2O
Molecular weight	1148.3	861.98	623.72	493.54
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	*P*-1	*P*-1	*P*-1	*C*2/*c*
Z	2	2	2	8
a (Å)	8.38964(15)	12.1100(8)	6.7561(12)	27.8283(5)
b (Å)	18.8780(3)	13.7781(9)	14.054(2)	7.02690(10)
c (Å)	20.4060(4)	14.6695(9)	16.203(3)	26.4417(4)
α (°)	114.1030(7)	63.125(3)	83.924(6)	-
β (°)	96.5800(8)	89.298(3)	83.276(7)	91.3430(7)
γ (°)	95.6500(8)	73.534(3)	79.140(7)	-
V (Å^3)	2892.83(9)	2074.4(2)	1495.0(4)	4582.69(13)
D_X (g/cm^3)	1.318	1.38	1.385	1.431
R_1	0.0726	0.1478	0.1373	0.0493

3.2.1. Molecular conformation and arrangement

Na-containing B-PAT I of the cis form

Fig. 3 shows the *ORTEP* plot of Na-containing B-PAT I of the *cis* form which include, in the asymmetric unit, three full phenol molecules and two half molecules. Four of these are hydrogen-bonded to the N atom of the 1,2,4-thiadiazol ring through OH···N hydrogen bonds, while the fifth phenol molecule remains free. It is remarkable to note that the central Na atom bridges two monoazo moieties in a *cis* fashion to make the molecule entirely flat (mean deviation from the least-squares plane with a methyl group from the *tert*-butyl substituent on the pyrazol ring above and below that plane: 0.0524 Å). Additionally, the four intramolecular NH···N hydrogen bonds also contribute to the planarity of the system. The occurrence of the *cis* form is quite unusual, because the *trans* form of the Na-free structure as formed by free rotation around C7-N6 or C9-N10 is more stable according to the MO calculations (Table 1). Nevertheless, the Na-coordination serves as the driving force to form the *cis* structure, as borne out by the MO calculations. The Na^+ cation is bound to three N atoms (N5, N7, and N11) of the triazine ligand, two from each pyrazole ring and one from the central deprotonated triazine ring system. Furthermore, the O atoms of a phenol and methanol molecule are also coordinated to the Na atom, respectively generating a five-coordinate Na-bisazo complex. The integration of the Na atom is due largely to the favorable distance of the Na position from N5, N7, and N11: Na1-N5 = 2.644(3), Na1-N7 = 2.420(3), and Na1-N11 = 2.642(3) Å. The distances of Na1-N5 and Na1-N11 are nearly equal, reflecting that the angle of N5/Na1/N7 and N7/Na1/N11 are 65.04(8) and 65.51(8)°, respectively.

Fig. 4 illustrates the molecular stack of Na-containing B-PAT I of the *cis* form along the *a* axis. The methanol and phenol ligands to the Na atom are positioned above and below the bis-azo skeleton. The polar bisazo molecules are arranged alternately in such a way as to effectively cancel their dipole moments to lower the lattice energy. In addition, two stacked columns are formed that are composed of the central Na(I) atom sandwiched by alternating two kinds of intermolecular hydrogen bonds: O (carbonyl oxygen: O1^{ii})...O-H (methanol: O8)/Na1/O-H (phenol: O2)...O (carbonyl

oxygen: $O1^{i}$). This forms two one-dimensional polymer-chains per molecule and assures a high thermal-stability of the compound.

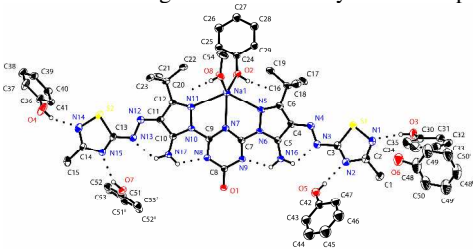

Fig. 3 ORTEP plot for Na-containing B-PAT I of the cis form.

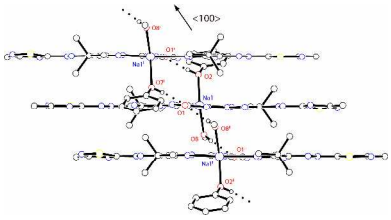

Fig. 4 Hydrogen-bond network of Na-containing B-PAT I of the cis form along the stacking a axis. [symmetry code(i): (-x, -y, -z) and (ii): (-1-x, -y, -z)]

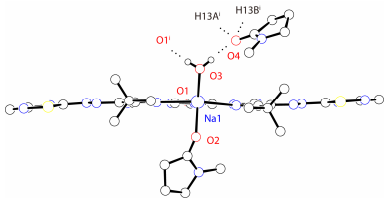

Fig. 6 Molecular side view of Na-containing B-PAT II of the cis form, [symmetry code(i): (1-x, 2-y, 1-z)]

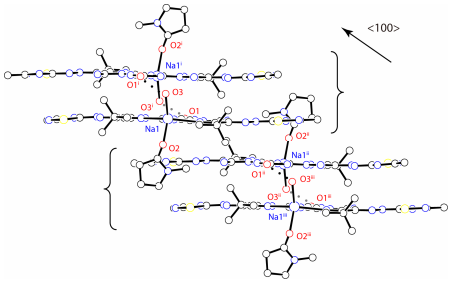

Fig. 7 Dimers of Na-containing B-PAT II of the cis form along the stacking a axis. [symmetry code(i): (1-x, 2-y, 1-z), (ii): (-x, 2-y, 1-z), and (iii): (-1+x, y, z)]

Na-containing B-PAT II of the cis form

Fig. 5 shows the *ORTEP* plot of Na-containing B-PAT II of the *cis* form with one solvated NMP. The geometry of the present five-coordinate Na-complex is quite similar to Na-containing B-PAT I except for the ligands arising from the solvent (*i.e.* coordinating solvents). The Na^{+} cation is bound to three N atoms (N5, N8, and N12) of the triazine ligand, two from each pyrazole ring and one from the central deprotonated triazine ring system. O2 from NMP and O3 from (water) complete the five-coordinate NaN_3O_2 coordination environment, although no water was added to the solution for recrystallization. In addition, O4 of solvated NMP is hydrogen-bonded to the H atom of the water molecule.

Fig. 6 illustrates the side view of the complex conformation, showing the arrangement of NMPs and water with respect to the triazinide plane. In addition, O4 is hydrogen-bonded to $H13A^{i}$ and $H13B^{i}$ of the amino group of the neighboring molecule through two intermolecular hydrogen bonds: O4···H13A-N13 and O4···H13B-N13 bonds. This bridges two Na-complexes to form a dimer, as shown in Fig. 7, together with two additional intermolecular O···HO hydrogen bonds between the carbonyl O atom of the triazine ring of one molecule and the H atom of the water molecule of the neighboring one. These dimers are stacked along <100>.

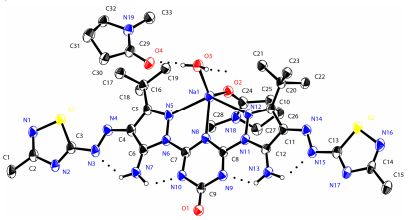

Fig. 5 ORTEP plot for Na-containing B-PAT II of the cis form.

Na-free B-PAT of the trans form

Fig. 8 shows the *ORTEP* plot of Na-free B-PAT of the *trans* form. The *trans* form is immediately formed upon elimination of the central Na atom through free rotation around C7-N6 or C9-N10. This occurs because the *trans* form is more stable than the *cis* form in the absence of the Na atom (*i.e.* Na-free B-PAT) according to the MO calculations (Table 1). There are five NH···N intramolecular hydrogen bonds formed between the NH of the amino group of the pyrazol ring and the N atom of the azo bond: N16-H16M···N3, N16-H16N···N8, N17-H17M···N13, N17-H17N···N7, and N9-H9···N11. The five intramolecular NH···N hydrogen bonds contribute to the planarity of the system.

Fig. 9 illustrates the in-plane dimer structure formed by two NH···O intermolecular hydrogen bonds: $O1\cdots H9^{i}$-$N9^{i}$ and N9-$H9\cdots O1^{i}$ bonds. The formation of dimers doubles the molecular unit to significantly stabilize the solid state. The present dimer is intrinsically formed without any intermediator such as solvents in the case of B-PAT II of the *cis* form.

As expected, Na-free B-PAT of the *trans* form exhibits now sufficient solvent-fastness, in addition to the light- and heat-stability. This may result presumably from the structural change.

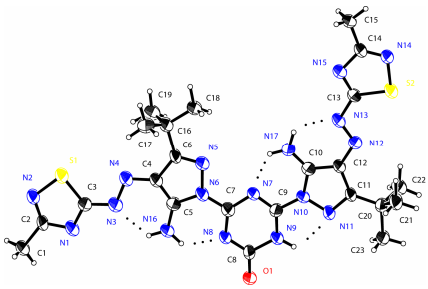

Fig. 8 ORTEP plot for Na-free B-PAT of the trans form.

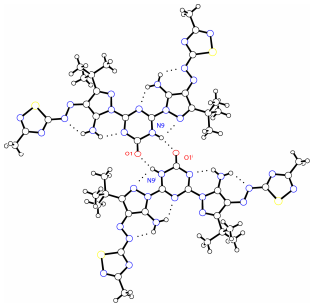

Fig. 9 Dimeric structure of Na-free B-PAT of the trans form. [symmetry code(i): (1-x, 2-y, 1-z)]

Na-free M-PAT

Fig. 10 shows the *ORTEP* plot of Na-free M-PAT. The formation of three intramolecular hydrogen bonds: N2-H2···N5, N10-H10M···N7, and N10-H10N···N3, stabilizes a planar conformation of the molecule. The water molecule is hydrogen-bonded to the O3A atom of the NMP molecule. In turn, the O4 atom is hydrogen-bonded to the H10M-N10 amino group of the monoazo skeleton. In addition, the O4-H4B group is weakly hydrogen-bonded to both N7 and N8. At both ends of the long molecular axis of the main molecule, the molecules are arranged in a head-to-tail fashion on the molecular plane with intermolecular N1-H1···N9 hydrogen bonds. These form a one-dimensional polymer chain on the molecular plane along the long molecular axis: <110> or <1-10> direction.

As shown in Fig. 11, the monoazo molecules are alternately stacked along the <010> direction in such a way to cancel their dipole moments so as to electrostatically stabilize themselves in the crystal. Each alternating pair is linked through a set of three-consecutive intermolecular hydrogen bonds. On one side of the molecule: N2-H2 (triazine ring)···O3A^{i} or O3B^{i} (NMP), O3A^{i} or O3B^{i} (NMP)···H4A^{i}-O4^{i} (water), and O4^{i} (water)···H10M^{i}-N10^{i} (amino group). An equivalent set of H-bonding interactions are found at the opposite sides of the molecules.

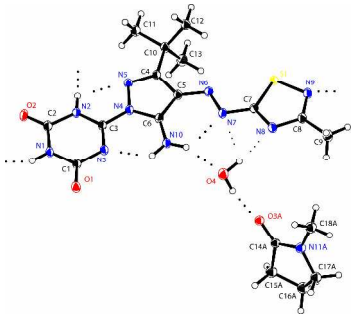

Fig. 10 ORTEP plot for Na-free M-PAT.

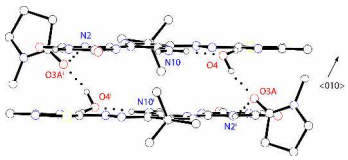

Fig.11 Dimer of Na-free M-PAT. [symmetry code(i): (1/2-x, 1/2-y, 1-z)]

4. Conclusions

Structure analysis has been carried out on four different crystals derived from the title compound. The conclusions can be summarized as follows.

1. The reported B-PAT is found to be a mixture of mono and bisazo compounds.
2. Two kinds of Na-containing B-PAT of the *cis* form and Na-free M-PAT were isolated as single crystals. $NaNO_2$ used for the preparation of diazonium components is responsible for the Na-complex formation.
3. Na-containing B-PAT is a five-coordinate Na-complex of the *cis* form. The central Na atom bridges by force two monoazo moieties to give a *cis* arrangement. Elimination of the Na atom yields a Na-free B-PAT of the *trans* form.
4. Na-containing or Na-free B-PATs as well as Na-free M-PAT are characterized by the formation of NH···N intramolecular hydrogen bonds which make the molecule entirely flat. Na-containing B-PATs of the *cis* form are dimerized through solvent ligands along the stacking axis (*i.e.* extrinsic dimer); whereas two Na-free B-PATs of the *trans* arrangement form an in-plane dimer through two NH···O intermolecular hydrogen bonds between the NH group of one molecule and the carbonyl O atom of the neighboring one (*i.e.* intrinsic dimer). Na-free M-PAT is characterized by the formation of NH···N intermolecular hydrogen bonds on the molecular plane in a "head-to-tail" fashion.

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Author Biography

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