

Full Length Research Paper

Isolation and characterization of the organic components of a black indigenous mineral hair dye

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Isolation and characterization of the main organic component of a black indigenous mineral dye; Yombotumtum (YT) was carried out. The methods employed include physicochemical characterization using solubility test, melting point, combustion test, organic and inorganic (ash) contents, functional group tests, IR and UV- VIS spectroscopic analysis and preparation of derivatives. The results obtained were compared with similar results when a synthetic organic compound reference was used.

Key words: Indigenous, mineral dye, organic components, physicochemical characterization and Spectroscopic analysis.

INTRODUCTION

Organic dyes and pigment commonly used in traditional painting have been limited to selected natural materials. Dyes are basically of two types namely natural dyes and synthetic dyes. Natural dyes include plant dyes, animals and mineral dyes. Plant dyes can be obtained from roots, flowers, leaves, fruits and bark of plants such as wood and indigo. Some animal sources of dyes include insects such as Cochineal, found on Cacti in Mexico, Lac found in India and Iran and kermes, found on oak tree near the Mediterranean. Mineral dyes come from ocher (yellow, brown, red); limestone or lime (white), manganese (black), cinnabar and lead oxide (red) azurite and lapis lazuli (blue), and Malachite (green) (Wayne, 1994).

Henna which is made from the powdered leaves of a desert shrub called lawsonia, has been used for thousands of years to colour hair and skin (Alice and Ithaca, 2003). The shift away from chemical dyes is enforced by the relatively high risk of sensitization to chemical dyes, in both hairdresser and their clients. Henna is derived from a shrub *Lawsonia inermis* which is native to the Middle East and North Africa (James and Vincent, 2004). The henna plant (*Lawsonia inermis*) is the mother of hair dyes. It varies in effect depending on where it grows. It has been reported that Moroccan henna is the lightest in colour, while Iranian henna is the richest and probably the most expensive. The leaves are

dried then crushed into fine powder and mix with water (Harris et al., 1995).

P-Phenylenediamine (PPD) is an aromatic amino compound used in almost every hair dye on the market, regardless of brand. Para-Phenylenediamine is a colourless slightly pink, gray or yellow crystalline solid (lumps or powder). On oxidation, usually through exposure to air, it turns red, brown then finally black. PPD is essentially a dye and chemical intermediate (Farrow, 2002). It may also be found in textile or fur dyes, dark coloured cosmetics, temporary tattoos, photographic developer and lithography plates, photocopying and printing inks, black robber, oils, greases and gasoline (Ngan, 1999).

Azo dyes are synthetic organic colourants which are characterized by great structural variety. Synthetic azo dyes are used extensively as dyes for textiles, food and cosmetics. Azo compounds can be intensely yellow, orange, red, brown, blue or even green depending upon the exact structure of their molecules. The azo compounds are of tremendous importance as dyes in industries today and as the acid-base indicators used in our research activities (Lockie and Geddes, 1992).

We reported recently investigation on the biochemical effects (Adebayo et al., 2005, Adebayo et al., 2006) and spectro-analytical characterization (Adebayo et al., 2007) of the mineral dyes Yombofitta (YF) and Yombo-tumtum (YT). In the present study, effort has been made to isolate and characterize the organic components of the mineral hair dye, Yombo-tumtum (YT), using basic chemical functional groups tests and spectroscopic data

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of the isolated compound and their derivatives.

MATERIALS AND METHODS

Source of the dye

The sample of rock-like black mineral dye was obtained from a local market in Ilorin, Kwara State, Nigeria. The local name of the dye is Yombo-tumtum (YT). The original source of the sample was traced to the coastal area of Ghana. This mineral dye is widely used for various purposes including dyeing of hair and clothing materials in the West African Sub-region.

Measurement of pH of the aqueous solution of the dye

The pH of aqueous solution of YT was determined using Griffin pH meter. The determinations were done in triplicates and the average values were recorded.

Determination of percentage of organic and inorganic components

1g of the dye was put in a crucible and ashed in the Muff furnace, the ash that was left in the crucible after cooling was weighed and used to determine the percentages of organic and inorganic components of the dye.

Recrystallization of PPD and YT in diethyl ether

The recrystallisation of PPD and the rock sample was carried out in warm diethyl ether. From approximately 1.0 g of the sample dissolved in 50 ml of diethyl ether, 0.217 g (21.7%) and 0.208 g (20.8%) of Pinkish/orange crystals of PPD_R and YT_R was obtained respectively. The melting points of the crystals were determined with Gallempkamp melting point apparatus.

Infrared IR and UV-VIS Spectroscopic analysis

IR Spectra of the raw and recrystallized dye were run on IR spectrophotometer Perkins Elmer model 457A. The UV-VIS spectra were also run on UV-VIS spectrophotometer Aquamate V4.60

Functional group test

The following functional groups tests were carried out on the dye: Unsaturation, alkanolic, phenolic, aromatic amine, nitro and halide groups using conventional methods (Sharma and Sharma, 1988).

Oxidation reaction

0.5 g of the dye was put in a beaker and 25 ml of hydrogen peroxide was added and mixed together. The mixture was kept for 24 h. After 24 h this mixture was filtered. The filtrate was treated with 25 ml of diethyl ether and shaken very well. Two immiscible solution resulted which were separated using separating funnel. Anhydrous magnesium sulphate was added to the diethyl ether layer and filtered. The filtrate was collected in a clean beaker and allowed to evaporate to dryness. The second layer was also put in a clean beaker and silica gel was added and was left to dry. After drying, ethanol was added, stirred very well and filtered; the filtrate was allowed to evaporate to dryness. The diethyl ether layer and the aqueous layer solid crystals were analyzed with IR spectrophoto-

meter Perkins Elmer model 457A.

PREPARATION OF DERIVATIVES

Preparation of azo dye

0.76 g of the dye was diazotised by dissolving in a mixture of concentrated hydrochloric acid (15 ml) and distilled water (30 ml). The solution was cooled with ice to 0°C and a cold solution of sodium nitrite (2.13 g in 25 ml of water) was added dropwise with continuous stirring for 10 min. 2-Naphthol (1.8 g) dissolved in 2 ml sodium hydroxide solution 50 ml was cooled to 5°C by immersion in an ice bath. The diazotised solution prepared above was added slowly with vigorous stirring for 1 h. The crude product was recrystallized from hot boiling ethanol to yield a fine reddish brown dye. (Ukponmwan et al., 2003). The melting points were determined and the azo derivative was analyzed with IR spectrophotometer Perkins Elmer model 457A.

Preparation of diazo dye

0.5 g of the dye was dissolved in 25 ml glacial acetic acid and cooled to 0°C. 10% ice-cold sodium nitrite (5 ml) solution (0.5 g in 4.5 ml of water) was added dropwise with continuous stirring for 10 min. 0.9 g of 2-naphthol was dissolved in 25 cm³ of warm 1 M sodium hydroxide solution and cooled to 5°C which was added slowly to the diazo solution (of dye) with vigorous stirring for 1 h. The resultant crude azo dye was diazotised again by adding dilute adding dilute hydrogen chloride (30 ml of H₂O and 15 ml of HCl). The solution was cooled to 0°C and a cold solution of sodium nitrite (2.13 g in 25 ml of H₂O) was added dropwise with continuous stirring for 10 min, brown solution results. 2-Naphthol (1.8 g) dissolved in 2 M sodium hydroxide solution 50 cm³ was cooled to 5°C by immersion in an ice bath. The diazotised solution prepared above was added slowly with vigorous stirring for 1 h.

The crude product was recrystallised from hot boiling ethanol to yield a fine reddish brown dye (Ukponmwan et al., 2003). The diazo derivative was also analyzed with IR spectrophotometer Perkins Elmer model 457A.

Melting point determination

The melting point of the recrystallised raw dye, PPD and their derivatives were determined using the Gallenkamp heated block apparatus, thermometer and capillary tubes.

RESULTS AND DISCUSSION

Physicochemical characterization of the dyes

Solubility test

The results of solubility of the sample in fourteen different solvents have been reported. The colour observed was attributed to the existence of certain complexes involving some elements within the sample and organic species acting as ligands (Adebayo et al., 2006).

Table 1 shows some of the physicochemical properties of the dye. The dye is rock-like in nature with distinct black colour. The pH of aqueous solution of the dye revealed that it is slightly alkaline. The alkalinity has been attributed to the presence of organic compound such as

Table 1. Physiochemical Parameters, Obtained For The Raw Dye (YT).

Test performed	Results
Appearance of the crystal	Black
pH of the aqueous solution	8.3
Max. absorption λ_{\max}	461.5 nm
Ash Content	53%
Organic content	47%
Melting point of PPD	138 - 141 °C
Melting point of recrystallized dye	128 - 138 °C

Other Physiochemical Parameters Obtained For the Raw Dye (YT).

Table 2. IR spectra (cm^{-1}) of raw sample YT.

YT	Tentative Assignment
702.3(s)	Aromatic Ring substitutions
818.8 (s)	PF ₂ S ₂ , C-C-O Sym. Stretch Aromatic Rings Mode
943.2 (w)	Mo-O Stretching
1016.1 (w)	Aromatic C-H
1064.8 (w)	Chelate ring
1119.4 (s)	C - O Chelate ring stretch
1235 (w), 1259.3 (s)	Coordinated amine C-N str
1308(m), 1380.9(s) ¹ , 1460(m)(a) ¹ .	Solvent nujol
1508 (w)	C-O Stretching, NO ₂ asym stretch, aromatic,
1630.2 (m)(sh)	Aromatic C=C
1745.7(s)(w), 1861.1(s)(w)	Aromatic overtone/combination
2724.6 (w)	Aromatic C-H
2931.3(b, ¹)	Solvent nujol, C-H str of CH ₃ .
3198.7(w) (b)	O-H Stretching of coordinated water in chelate complex.
3308.2(w)(b)	O-H Stretching of coordinated water in Chelate complex.
3369(w)(sh)	-N-H. Stretching.

Intensities in parenthesis: b-board, vs-very strong, s-strong, m-medium, W-Weak, Super Script 1 - Spectra due to solvent used. Sh-sharp.

amine or thiols or inorganic compound such as carbonates or bicarbonates of alkaline and alkaline earth metals in the mineral dye (Adebayo et al., 2006). The λ_{\max} , 461.5 nm of the aqueous solution of the dye indicates absorption in the visible regions showing the presence of chromogens and other unsaturated compounds in the dye. The percentage of organic and ash contents of the dye (47% and 53% respectively) revealed complex nature of the dye.

SPECTROSCOPIC ANALYSIS

Infrared (IR) Spectroscopy Measurement of raw sample YT

The results of IR analysis of the raw sample are presented in Table 2. The absorptions at 1374.7, 1380.9, 1460, 2925.1 and 2931.3 cm^{-1} might probably be due to the sol-

vent (John, 1971). These wave numbers were marked with superscript (1) in the table. IR band of 1630.2 cm^{-1} from sample YT can be attributed to C = O stretching frequencies of some metal chelates in the samples (Junge and Musso, 1968). The 1514.60 cm^{-1} and 1235 cm^{-1} from sample YT can be assigned to C = C chelate ring, C - C stretching and C = O stretching respectively of some metal chelate complexes within the sample. The $\nu_{\text{asym}} \text{C} = \text{O}$ has been reported to be dependent on the inductive effect of the constituents, such as electron withdrawing which increase $\nu_{\text{asym}} \text{C} - \text{O}$ and electron releasing, which decrease its relative value to that of the ligands (Behnke and Nakamoto, 1966; Nakamoto, 1970).

Hence, the little variation in the spectra observed might be due to some substituents that may be present in the sample e.g NO₂ or C₆H₅ groups. In one of the studies reported in the literature (Ferraron, 1971), IR broad peaks in region of 3300 - 3550 cm^{-1} could be assigned to OH

Table 3. IR Spectra of Recrystallized PPD and sample YT in diethyl ether (cm^{-1}) (PPD_R and YT_R).

PPD _R	YT _R	Tentative assignment
687.9		Aromatic rings mode
814.2	809.5	ditto
1037.9	994.2	C-N stretching of aromatic NO ₂
1125.6	1135.3	C-NO ₂ of Aromatic rings
1524.3	1519.6	ditto
1699.4	1699.4	C-H stretch aromatic overtones
2380.5	2380.5	ditto
3397	3406.7	N-H stretching
3742.3	3737.6	Ditto

stretching frequency of coordinated water in chelate spectra of Ba (II), Mn(II), Co(II), Ni(II), Zn(II) and Na. Hence I.R bands, 3198.7 (b), 3308.2 (b) 3369 (w.sh) cm^{-1} from sample YT were likely due to coordinated water of some of the complex compounds in these sample. This observation is evident from the physical nature of the mineral. It has also been reported (Okafor, 1981) that in the anhydrous complexes, the band between 3080 - 3600 implies the presence of (-N-H), hence the 3369 cm^{-1} (sh) from YT might be due to the presence of the -N-H. Also the range 1230 - 1260 cm^{-1} has been observed to be characteristic of coordinated amine group and associated with $\nu(\text{C-N})$ which occurs at 1276 cm^{-1} .

This band is to be expected since nitrogen cannot be ruled out of the mineral as it is being used as hair dye. An IR spectrum near 1000 - 1100 cm^{-1} has been attributed to cyclopentadienyl complexes of transition elements possessing an unsubstituted ring. The presence of bands 1016.1 and 1064 cm^{-1} from sample YT can therefore be assigned to chelate ring formed between the metals and of organic components of the sample. The I.R band 944 cm^{-1} ν (Mo-O) stretching has been reported (Okafor, 1981) for the compound CsMoO₂F₄. Compared with 943.2 from sample YT, one can rightly suspect this compound in this sample. The band 818.8 cm^{-1} for YT may be attributed to PF₂S₂ salts (Ferraron, 1971) and therefore, the possibility of this kind of compound within the sample.

The IR of recrystallized PPD and YT (Table 3) show bands 3397 - 3742.3 cm^{-1} that have been assigned to NH stretching of primary amine. The bands 871, 831 and 762 cm^{-1} have been assigned to aromatic substitution (Ukoha et al., 2005) hence the presence 687.9 and 814.2 cm^{-1} from PPD and 809.5 cm^{-1} from YT may be due to the aromatic nuclei. The medium and strong bands at 1037.9, 994.2, 1125.6 and 1135.3 can be attributed to C-N stretching of aromatic NO₂ compounds. Also, the band 1524.3 from PPD and 1519.6 from YT could be attributed to C-NO₂ of aromatic ring as such has been assigned to asymmetric stretch of an aromatic nitro group (Edward and Richard, 1980; Brian, 1999). This group may be expected from partial oxidation of the reference compound PPD

Table 4. Functional Group Test Results.

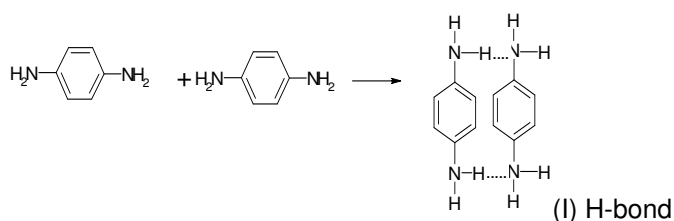
Function group	
Unsaturation	+
Phenolic group	+
Aromatic amine	+
Aromatic nitro	+
Aromatic halide	+
Carboxylic group	-

Key + = Present.
- = Absent.

and similar oxidation of the sample since the IR analysis were not in situ or immediate. The bands 1699.4 and 2380.5 cm^{-1} may likely be due to the C-H stretch aromatic overtone/combination of 814.2 and 809.5 cm^{-1} and 1125.6, and 1135.3 cm^{-1} for PPD and YT respectively.

Melting points

The melting points of the recrystallized sample YT (130 - 138 °C), though a wide range may be acceptable for comparison with the melting point of PPD (138 - 141 °C). There can also be possibility of intermolecular association of molecules of PPD or its derivatives in the samples through nitrogen atom of one molecule and the hydrogen atom of another molecule forming H-bond (I) between them which may also contribute to variation in melting point.



UV-Vis Spectroscopic measurement

The results of the absorption spectra 461.5 nm of the raw dye show that the raw dye absorbed at visible region which indicate the possibility of certain chromogens within the dye (William, 1986).

Functional groups test

Table 4 shows the results of the functional group tests carried out on the raw dye. The results show that the sample contain aromatic nucleus. This is evident from the unsaturation tests, the sample solution decolourised acidified KmnO₄ and solid sample give a very sooty flame when burnt in non-luminous flame. It was also show that the sample contains aromatic amine, halides and nitro.

The nitro groups may be due to partial oxidation of the amine group to nitro group.

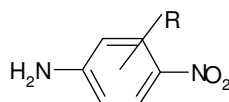
Table 5. Oxidation products PPD, YT+H₂O₂ (i) Diethyl ether extract.

PPD ₀₁	YT ₀₁	Tentative assignment
814.2	673.1,814..2	Aromatic ring substitutions
945.5	1028.2	C-N str. of aromatic NO ₂ .
1106.1,	1120.6	C-NO ₂ of Aromatic rings.
1159.5		C-N bending
1300.6	1344.3	C-H bending
1456.2	1465.9	Aromatic C-H str.
1553.5, 1631.4	1553.5, 1650.9, 1699.4	Aromatic C-NO ₂
1748, 1894.1	1748, 1889.1	Aromatic overtones/combinations
	2030.2, 2059.4	C-N str.
3474.9, 3752.0	3538.1	N-H str.

Table 6. Oxidation products PPD, YT + H₂O₂ (ii)Aqueous layer (ethanol extract).

PPD ₀₂	YT ₀₂	Tentative assignment
814.2	814.2	Aromatic ring substitutions
999, 1140.1	1125.6	C-NO ₂ of Aromatic rings.
1344.3	1339.6	C-H bending.
1650.9	1504.9	Aromatic NO ₂
1748	1709.1,1743.3	Aromatic overtones/combinations.
2341.6	2375.5	-C = N str.
3469.9, 3849.4.	3469.9, 3732.6.	N-H or O-H str.

The results of oxidation reaction of reference compound, PPD with that of the sample suggested that the amine of the sample have being converted to nitro. The presence of NH₂ amine was confirmed by the result of azo dye derivatives prepared from the reference compound PPD and the sample which gave similar results.



(II)

Where; R may be CH₃, OH, C=O, NH₂ etc. The tentative structure of PPDO₁, YTO₁

IR of 30% H₂O₂ oxidation products of PPD and YT (diethylether extract, PPDO₁ and YTO₁)

Table 5 shows the IR spectra of YTO₁ and PPDO₁. The peaks 814.2 cm⁻¹ from YTO₁ and PPDO₁ and 673.1 from YT indicate the presence of C-H bending of aromatic ring. The peaks 1980 – 1745 cm⁻¹ has been assigned to aromatic overtones/combination (Edward and Richard, 1980), hence, the absorption bands at 1894.1 and 1748 from YTO₁ and PPDO₁, may be due to aromatic overtones/combinations. The weak bands at 1553.5, 1650.9 and 1699.4 cm⁻¹ from YTO₁ and 1631.4 cm⁻¹ from PPDO₁ which could be assigned to C-NO₂ stretch (John, 1971). Other bands 3474.9 - 3752.0 cm⁻¹ may be due to incomplete oxidation reactions.

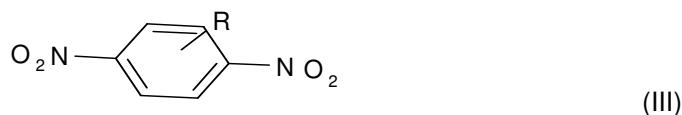
IR Data of 30% H₂O₂ oxidation products of PPD and YT (ethanol extract, PPDO₂, YFO₂ and YTO₂)

Table 6 shows the IR spectra of YTO₂ and PPDO₂. The bands at 814.2 from YTO₂ and PPDO₂ can be assigned to C-H bending. The peaks between 1570 – 1500 cm⁻¹ and 1370 – 1300 cm⁻¹ have been assigned to C-NO₂ stretch (John, 1971). Therefore, peaks 1504.9 cm⁻¹ and 1339.6 cm⁻¹ from YTO₂, 1548.8 cm⁻¹ and 1344.3 cm⁻¹ from PPDO₂ may indicate C-NO₂ stretch.

However, peaks 3469.9 cm⁻¹, 3406.7 cm⁻¹ and 3241.4 cm⁻¹ from YTO₂ and 3469.9 cm⁻¹ from PPDO₂ could be due to N-H or O-H stretch. The presence of N-H might be due to incomplete oxidation of NH₂ and the presence of O-H might be from traces of water from aqueous layer (III).

Table 7. Azo derivatives of PPD and YT with β -naphthol 1:1.

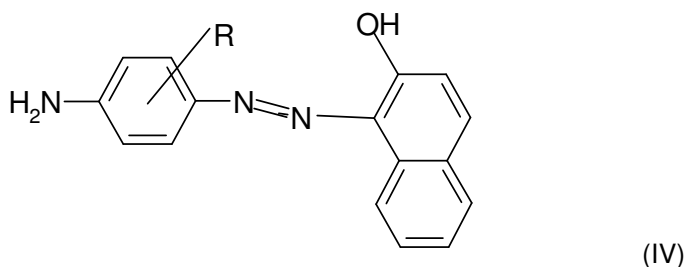
PPDA ₁	YTA ₁	Tentative assignment
857.9	857.9	Aromatic ring substitutions
1135.3	1135.3	C-NO ₂ of Aromatic rings.
1650.9	-	-N = N- bending vibration.
1748	1709.1, 1748	Aromatic overtones/combinations.
2375.5	2380.5	-C = N str.
3411.5,	3401.7,	
3742.3,	3742.3	N-H or O-H str.



Where; R may be OH, NH etc. The tentative structure of PPDO₂, YTO₂

IR of Azo derivatives of PPD and YT couple with β -naphthol (1:1)

The IR absorption spectra of the YTA₁ and PPDA₁ are shown in Table 7. The peaks 3401.7 cm⁻¹ from YTA₁ and 3411.5 cm⁻¹ from PPDA₁ can be due to O-H stretch or N-H stretch. The peaks 1748 cm⁻¹ from YTA₁ and PPDA₁ can be attributed to aromatic overtones/combinations (Edward and Richard, 1980). However, the moderate absorption band at 1626.4 cm⁻¹ from YTA₁ indicates the -N = N- stretching vibrations as the peaks between 1630 cm⁻¹ and 1575 cm⁻¹ has been attributed to -N = N- stretching vibrations of azo compounds (John, 1971). The peaks 857.9 cm⁻¹ from YTA₁ and PPDA₁ are likely due to C-H stretch of aromatic ring. The peaks 2375.5 and 2380.7 have been assigned to -C = N. Other peaks 3401.7 - 3742.3 cm⁻¹ may be due to stretching vibration of OH and NH from the β -naphthol or incomplete diazotization of NH₂ groups of the sample and PPD (IV).



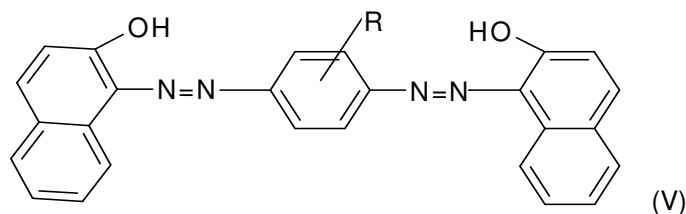
Proposed structure for PPDA₁ and YTA₁ IR of Azo derivatives of PPD and YT couple with β -naphthol (1:2)

Table 8 shows the IR spectra of YTA₂ and PPDA₂. The peak 3525 - 3200 cm⁻¹ has been assigned to O-H stretch

Table 8. IR of Azo derivatives of PPD and YT couple with β -naphthol (1:2).

PPDA ₂	YTA ₂	Tentative assignment
697.6, 843.4.	687.9, 809.5	Aromatic ring substitutions.
1004	1113	C-NO ₂ of Aromatic rings.
1456.2	1378.5	Aromatic C-H str.
1660.6	1626.4	-N = N- bending vibration
2973.8	2983.5	C-H str.
3338.6,	3406.7,	N-H or O-H str.
3761.8	3747.3.	

ching (Edward, 1980). Hence the 3411.5 cm⁻¹ from YFA₂, 3406.7 cm⁻¹ from YTA₂ and 3338.6 cm⁻¹ from PPDA₂ can be due to O-H stretching. Furthermore, the absorption bands at 1378.5 cm⁻¹ from YTA₂ indicate O-H bending as the peaks 1350 \pm 50 cm⁻¹ has been assigned to O-H bending (Brian, 1999). Also peak 1255 - 1000 cm⁻¹ has been attributed to C-O stretching (Edward, 1980), hence peaks 1135.3 cm⁻¹ and 1113 cm⁻¹ from YTA₂ and 1149.8 cm⁻¹, 1101.1 and 1004 cm⁻¹ from PPDA₂ can be assigned to C-O stretching. The peaks 1630 - 1575 cm⁻¹ and 1660 - 1630 cm⁻¹ have been assigned to -N = N- and C = N- stretching vibrations respectively (John, 1971). Hence, peaks at 1626.4 cm⁻¹ from YTA₂ and 1660.6 cm⁻¹ from PPDA₂ could be due to -N = N- and C = N- stretching vibrations (V). Also, the absorption peaks, 809.5 cm⁻¹ and 687.9 cm⁻¹ from YTA₂ and 843.4 cm⁻¹ and 697.6 cm⁻¹ from PPDA₂ can be assigned to C-H stretching.



The proposed structure for YTA₂.

Conclusion

It is evident from the study that the important organic moiety in the sample of the mineral dye is p-phenylenediamine or its derivatives. This compound is one of the major ingredients of commercial hair dyes, hence the used of the dye as hair dye.

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