

COLOUR IN RELATION TO CHEMICAL CONSTITUTION OF THE ORGANIC AND INORGANIC SALTS OF ISONITROSO-DIPHENYL-THIO- BARBITURIC ACID AND ITS HIGHER HOMOLOGUES AND ANALOGUES.

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ISONITROSO-MALONYL-UREA or violuric acid, which forms interesting coloured salts with alkali hydroxides and organic bases, has been exhaustively examined by Ghatak and Dutt,¹ who found that the stronger the basic character of the base, the greater is the intensity of the colour of the salt that is formed in combination with violuric acid. They examined the absorption spectra of the organic salts of violuric acid along with their dissociation constants and came to the conclusion that there is a general relationship between the two values although no hard and fast mathematical relationships could be derived from them. Previous workers in this field, namely, Hartley,² Hantzsch,³ Meek and Watson⁴ had only confined their attention to the absorption spectra of free violuric acid and the sodium and potassium salts in water. They had already taken notice of the fact that in dry non-hydroxylic solvents, violuric acid was quite colourless, but in hydroxylic solvents, as well as in wet non-hydroxylic solvents, it had a distinct pink coloration.

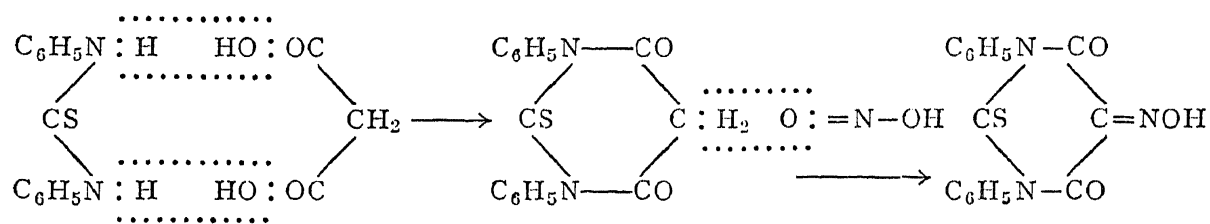
Later on Gaiind and Dutt⁵ took up the study of violantin and alloxantin and their organic salts and found that the intensity of their coloration was even greater than the corresponding compounds of violuric acid. Both the compounds are monobasic in nature and form well-defined salts very similar to those of violuric acid, with the difference that unlike the latter, the former undergo hydrolytic decomposition in water. Consequently, the dissociation constants could not be determined and the absorption spectra were found in alcoholic solution.

The next interesting work in this connection was done by Lal and Dutt,⁶ who took up the study of *isonitroso-thio-barbituric acid* or *thio-violuric acid*,

which was prepared by them for the first time by the action of nitrous acid on thio-barbituric acid. The alkali and organic salts of this compound were found to be highly coloured substances, yielding fluorescent and intensely purple solutions with absorption bands between 5900–6025 Å. They were in this respect far more coloured than the corresponding salts of violuric acid, and it appeared highly interesting to note the tremendous difference in colour and absorption brought about by the introduction of an atom of sulphur in the molecule of violuric acid in place of an atom of oxygen. The effect of sulphur on the colour of organic compounds and dyestuffs has previously been noticed by former workers, *e.g.*, by Purvis, Jones and Tasker,⁷ who noticed that the thio-oxalates of alkalis are yellow in colour, whereas the corresponding oxalates are colourless; by Dutt and Watson,⁸ who have shown that many mercaptan derivatives of azo-dyes and thio-fluorescein are deeper in colour than the corresponding dyes containing oxygen in place of sulphur; by Reid and his collaborators⁹ who also worked in similar lines to Dutt and Watson; and by Dey and Dutt,¹⁰ who worked on dyestuffs prepared from thio-diglycollic acid. But in none of these works mentioned above was the intensity of colour found to be so much enhanced by the introduction of an atom of sulphur in place of an atom of oxygen, as in the case of compounds derived from thio-violuric acid. Lal and Dutt examined the absorption spectra of these compounds and also the dissociation constants of a number of them which were soluble in water, but on comparing the results thus obtained, they came to the conclusion that the colour of thio-violurates is not intimately connected with electrolytic dissociation, and in fact intense colours were possessed by compounds which were altogether insoluble in water or hydroxylic solvents, and whose absorption spectra had to be determined in acetone or chloroform solutions.

On account of the interesting results obtained with thio-violuric acid, it was naturally expected that any further loading of the molecule of the substance with heavy substituents might result in the production of a compound capable of yielding salts with even greater intensity of colour than that obtained from thio-violuric acid. This expectation from the theoretical point of view has now been realised in the case of 1 : 3-diphenyl-thio-violuric acid. It is the aim of the present investigation to examine the effect of loading on the molecule of thio-violuric acid by the introduction of two phenyl or even heavier groups, and also to compare their salts with the corresponding salts of diphenyl-violuric acid, which would differ from the former only in possessing an atom of sulphur in place of the oxygen atom.

1 : 3-Diphenyl-thio-violuric acid has now been prepared for the first time by the action of nitrous acid on 1 : 3-diphenyl-thio-barbituric acid, which in its turn has been obtained by the condensation of thiocarbanilide with malonic acid in presence of acetyl-chloride.

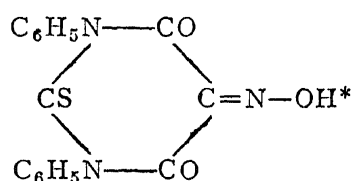


Thiocarbanilide Malonic acid.

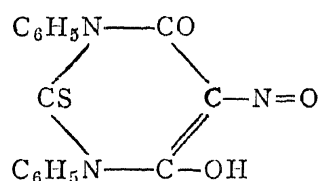
Diphenyl-thio-barbituric acid.

Diphenyl-thio-violuric acid.

Isonitroso-diphenyl-thio-barbituric acid or diphenyl-thio-violuric acid is a monobasic acid and may be represented by formula (1) shown below, in which the hydrogen atom marked with an asterisk is replaceable by metal. This is the *oximino-ketonic* form :



(1) Oximino-ketonic form.



(2) Nitroso-enolic form.

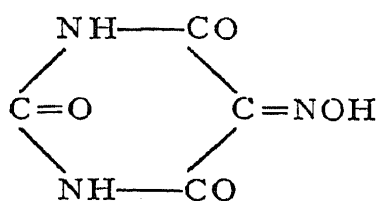
But an alternative structure can be formed due to the tautomerism of the marked hydrogen atom to give the *nitroso-enolic formula* (2), which is equally capable of existence. This contains the highly strained grouping $\text{N} = \text{O}$, and hence according to the "Theory of colour on the basis of molecular strain" advanced by Dutt,¹¹ it must be a highly coloured substance. On the other hand if the oximino-ketonic formula be correct, then diphenyl-thio-violuric acid should not have any colour at all, or at best only a pale yellow colour. We find that the compound in question is an orange coloured solid dissolving in solvents like acetone to an orange solution. It appears that in solution as well in the solid state, the substance exists mainly in the oximino-ketonic form. But this state of affairs becomes considerably modified when a salt formation of the acid occurs by treatment with alkali or an organic base. Under such circumstances, on account of the greater load of the substituting metal or basic radical, the tautomerism between the two above-mentioned forms will be far more difficult and the more highly strained configuration (2) will result as soon as its existence becomes possible due to the following reasons : The $-\text{CO}$ -groups in the molecule of diphenyl-thio-violuric acid are really the residues of carboxyl groups, and they still retain the acidic character

in a modified form due to the presence of the NPh-groups in the vicinity, whose basic character they have more than neutralised. When such a group enolises by the transference of a hydrogen atom, it becomes more acidic than a -NOH group (*cf.* uric acid and the ureides with the oximes of aldehydes and ketones). It can be easily seen therefore that in order to neutralise an alkali like sodium hydroxide or an organic base, the original weakly acidic oximino-ketonic form has to tautomerise into the more acidic nitroso-enolic form in order that a neutral salt formation may take place. And once the tautomeric hydrogen atom becomes substituted in the latter form, the nitroso-enolic structure becomes fixed due to salt formation, and on account of the heavy load cannot tautomerise back into the oximino-ketonic form. It is due to this that a highly strained but stable structure results, which is in fact responsible for the intense colour of the diphenyl-thio-violurates.

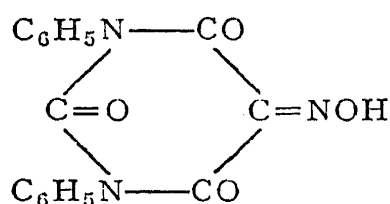
As a further proof of the above theoretical exposition of the colour phenomenon of the salts of diphenyl-thio-violuric acid, it may be pointed out that weak bases like aniline, picoline, quinoline, *isoquinoline*, etc., form molecular combinations with the acid in dry acetone solution which are only slightly coloured, *i.e.*, which are either yellow or orange. But in the presence of only a trace of water, true salt formation takes place immediately with production of the usual intense blue or green colorations. It is therefore quite evident that the real basic character of the base has to be developed in the presence of a minimum quantity of water before the true nitroso-enolic structure of diphenyl-thio-violuric acid with its concomitant highly acidic nature can be formed with a view to real salt formation. In other words, it is a question of ionisation of the base before the salt formation may take place. Very weak bases like β -naphthylamine, *m*-xylylene, etc., do not produce any salts for the same reason.

The effect of sulphur on colour as seen on comparison of the absorption spectra of salts of diphenyl-thio-violuric acid with the corresponding salts of diphenyl-violuric acid (Prakash and Dutt,¹² work just published) is also very interesting. Whereas the characteristic colour of the latter is purple-violet with the absorption maxima in the vicinity of 5900 Å, the characteristic colour of the former is bluish-green to deep emerald-green, with absorption maxima in the neighbourhood of 6500 Å in many cases. Besides this there is another aspect of the "Theory of colour on the basis of molecular strain" advanced by Dutt (*loc. cit.*), namely, "In a system that is under strain, the effect of load will be to increase the strain, provided it acts within close proximity of the strain; the further away the load is from the centre of the

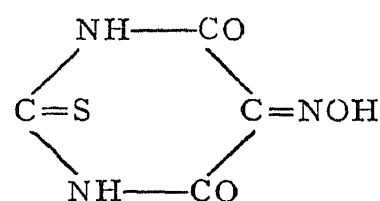
strain, the less will be the effect" exemplified, when we compare the four types of compounds given below :—



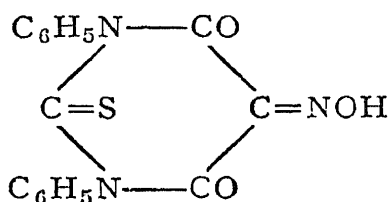
(3) Violuric acid. Pink salts,
Abs. Max. 5305 Å.



(4) Diphenyl-violuric acid. Violet
salts, Abs. Max. 5900 Å.



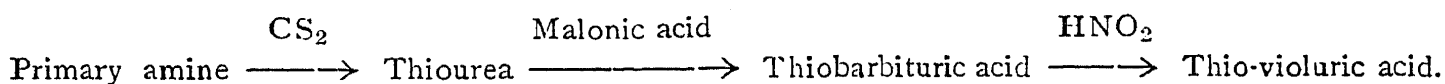
(5) Thio-violuric acid. Violet
salts, Abs. Max. 5900 Å.



(6) Diphenyl-thio-violuric acid.
Green salts, Abs. Max. 6500 Å.

We find that a load of 16 units is as effective in deepening the colour of violuric acid to thio-violuric acid, as a load of 154 units to the same substance under slightly different conditions, with formation of diphenyl-violuric acid. The reason is obvious on scrutiny, since we find that in the former case the load has been applied at the centre of the strain itself, *i.e.*, at the double bond. But in the latter case we find that the phenyl groups are one bond removed from the double bond, and are consequently less effective as loads in deepening the colour. Similar phenomenon will be observed when (3), (4) and (6) are compared together.

On account of the great success achieved with the preparation of diphenyl-thio-violuric acid and its organic and inorganic salts and, also the fulfilment of the expectations as calculated from the theoretical point of view with regard to this compound, attempts were made to prepare other derivatives of thio-violuric acid containing heavier substituents than the two phenyl groups. With this object in view, the following scheme was worked out with an equally great success :



The following primary aromatic amines were successfully used in this connection: *o*-toluidine, *m*-toluidine, *p*-toluidine, *m*-xylylidine, *o*-anisidine, *p*-phenetidine and α -naphthylamine, and the corresponding substituted thio-violuric acids obtained. All these higher homologues and analogues of diphenyl-thio-violuric acids with the exception of the α -naphthyl

compound yield more intensely coloured compounds with alkalies and organic bases than the corresponding ones obtained from diphenyl-thio-violuric acid, and their absorption bands are also higher up in the spectrum. This has been exactly according to expectations from the point of view of theoretical considerations. But in the case of the α -naphthyl compound, although the impure stuff yielded a green coloration with alkalies and organic bases, yet on purification and crystallisation, the substance was resolved into a compound giving only violet salts with them. Apparently this is the only anomaly in connection with the consideration of the large number of substances that have been examined in this investigation.

Experimental.

Preparation of diphenyl-thio-barbituric acid.—A mixture of thiocarbanilide (20 gm.), malonic acid (12 gm.) and acetyl-chloride (18 c.c.) was heated on the water-bath under reflux for about 30 minutes. The mixture first became a completely homogeneous fluid which ultimately solidified to a compact light yellow crystalline mass. The product was broken up, ground fine with water in a mortar, filtered, washed, dried and crystallised from glacial acetic acid in bright yellow prismatic needles melting at 245° C.

The acid is sparingly soluble in most of the ordinary organic solvents in the cold, fairly soluble in boiling alcohol and hot glacial acetic acid, almost insoluble in chloroform, benzene and ether and insoluble in water. It dissolves easily in dilute caustic alkalies and ammonia.

Preparation of isonitroso-diphenyl-thio-barbituric acid or diphenyl-thio-violuric acid:—Diphenyl-thio-barbituric acid (20 gm.) was dissolved in dilute sodium hydroxide (5 per cent.) and a solution of sodium nitrite (20 gm.) in the minimum quantity of water added. The mixture was filtered through thick cotton cloth, cooled with the addition of lumps of clear ice, and gradually acidified with the addition of ice-cold dilute sulphuric acid. The light buff coloured precipitate of the isonitroso compound was allowed to stand overnight, then filtered, washed with water, dried and crystallised from boiling glacial acetic acid, when it was obtained in the form of glistening orange rhombic prisms (see Plates IV and V) melting at 227° C.

Diphenyl-thio-violuric acid is absolutely insoluble in water, but dissolves in boiling glacial acetic acid to the extent of only about 3 per cent. and on cooling, practically the whole amount crystallises out. It is very slightly soluble in other neutral organic solvents, with the exception of acetone, in which it is fairly easily soluble, forming a bright orange non-fluorescent solution. On the addition of alkalies or organic bases, intense blue or green

colours are developed and in the majority of cases, the salt is precipitated in a crystalline and exceedingly beautiful form. The colour change is so sharp and rapid that diphenyl-thio-violuric acid can be used as an excellent indicator. The salts give absorption bands reaching much further into the red region than those given by the corresponding salts of thio-violuric acid. With the exception of the alkali salts, the rest are quite insoluble in water, but in acetone they are very easily soluble giving intense colorations which are augmented by the addition of a few drops of water and in this aqueous acetone medium, all the absorption spectra have been determined. All the salts of diphenyl-thio-violuric acid possess beautiful crystalline structure, are fairly stable, but melt with decomposition. The lowest decomposition temperature that has been recorded is in the vicinity of 130°C . Some of the alkaloid salts are rather unstable and become sticky and swell up due to decomposition, on keeping. Consequently they have to be prepared immediately before the examination of their properties. They all possess cubical crystalline structure. Contrary to expectation, they were found to be optically inactive, thus proving that racemisation took place along with salt formation. All the salts described in this paper have been prepared by mixing together equimolecular proportions of the acid and the base in acetone solution. In 90 per cent. of the cases, the salt crystallised out completely but, in the rest, it had to be obtained by evaporation of the mother liquor.

Preparation of the higher homologues and analogues of diphenyl-thio-violuric acid was done in a similar way to the above. For the sake of abbreviation, the properties of the barbituric and violuric acids (Table I), the salts of diphenyl-thio-violuric acid (Table II) and some of the salts of the higher homologues and analogues of diphenyl-thio-violuric acid (Table III) are given in tabular forms at the end of the paper. Microphotographs of the crystalline structures of diphenyl-thio-violuric acid and its higher homologues and analogues have also been appended showing the exceedingly fine crystalline nature of these substances.

Summary and Conclusions.

1. *Isonitroso-diphenyl-thio-barbituric acid* has been obtained for the first time by the action of nitrous acid on 1 : 3-diphenyl-thio-barbituric acid prepared in its turn by the action of diphenyl-thiourea on malonic acid in presence of acetyl chloride.
2. *Isonitroso-diphenyl-thio-barbituric acid* or diphenyl-thio-violuric acid has an orange colour in the solid state or in solution in organic solvents,

but on treatment with alkalies or organic bases, intense blue and green coloured salts are formed, the transition of colour being sufficiently strong and sharp for the substance to act as an excellent indicator.

3. The change of colour from orange to blue or green has been shown from theoretical considerations to be due to a fundamental change in the constitution of the molecule from an oximino-ketonic to a nitroso-enolic structure.

4. The above change in the molecular structure results in the production of a true nitroso-group, which from the point of view of a "Theory of colour on the basis of molecular strain" advanced by one of the present authors, has been shown to be the most highly strained amongst the chromophoric groups, and consequently produces the greatest intensity of colour.

5. The loading effect of the two phenyl groups as well as that of the sulphur atom from the point of view of colour production has been discussed, and it has been shown that the effect is quite in accordance with the theory of colour advanced by Dutt.

6. From the study of the absorption spectra of the salts of diphenyl-thio-violuric acid it has been found that their intensity of colour is roughly proportional to the strength of the basic character of the base entering into salt formation.

7. Further study of the absorption spectra of the salts of a series of newly synthesised higher homologues and analogues of diphenyl-thio-violuric acid indicates that the effect of additional load on the molecule of the substance is to produce still further intensification of colour as expected from theoretical considerations, the greatest effect being produced by substituents in *meta*-positions closely followed by those in the *para*.

TABLE I.
Properties of the Main Barbituric and Violuric Acids.

Name (T. B. = thio-barbituric T. V. = thio-violuric acids)	Colour of solid	Remarks	Colour in solution (aqueous acetone)	M.P.	Absorption Maxima λ	Analysis (% S. Theo- retical with- in bracket)
<i>1. The barbituric acids.</i>						
Diphenyl-T.B. ..	Pale yellow	Prisms	Yellow	245°	4650	10.62 (10.81)
Di- <i>o</i> -tolyl-T.B. ..	Yellow	Rectangular prisms	Yellow	190°	4650	9.67 (9.87)
Di- <i>m</i> -tolyl-T.B. ..	Light yellow	Fine needles	Yellow	265°	4550	9.52 (9.87)
Di- <i>p</i> -tolyl-T.B. ..	Bright yellow	Rectangular prisms	Yellow	233°	4650	9.58 (9.87)
Di- <i>m</i> -xylyl-T.B. ..	Yellow	Do.	Yellow	247°	4720	9.50 (9.09)
Di- <i>o</i> -anisyl-T.B. ..	Yellow	Fine needles	Yellow (deep)	248°	4720	8.35 (8.98)
Di- <i>p</i> -phenetyl-T.B. ..	Light salmon- pink	Do.	Deep yellow	167°	4720	8.75 (8.33)
Di- α -naphthyl-T.B. ..	Greenish-yellow	Cubical crystals	Orange- yellow	216°	4960	8.52 (8.08)
<i>2. The Violuric Acids.</i>						
Diphenyl-T.V. ..	Orange-red	Glistening hexa- gonal plates & prisms	Orange	227°	5130	9.95 (9.84)
Do. (No. 2) ..	Dull orange	Rectangular prisms & needles	Orange- yellow	220°	5050	9.30 (9.84)
Di- <i>o</i> -tolyl-T.V. ..	Buff	Rectangular plates	Yellow	200°	4755	9.04 (9.06)
Di- <i>m</i> -tolyl-T.V. ..	Dull orange	Rhombic plates	Orange	216°	5160	9.21 (9.06)
Di- <i>p</i> -tolyl-T.V. ..	Deep salmon- pink	Hexagonal plates	Reddish- orange	128°	5180	9.02 (9.06)
Di- <i>m</i> -xylyl-T.V. ..	Buff	Needles	Orange- yellow	165°	5060	8.85 (8.42)
Di- <i>o</i> -anisyl-T.V. ..	Deep mahogany- brown	Glistening cubes	Orange-red	212°	5220	7.81 (8.31)
Di- <i>p</i> -phenetyl-T.V. ..	Orange-buff	Spindle-shaped prisms	Do.	128°	5260	7.16 (7.74)
Di- α -naphthyl-T.V. ..	Violet-black	Glistening roundish poly- gonal crystals	Brownish- yellow	216°	5140	7.96 (7.52)

TABLE II.
Properties of Diphenyl-thio-violurates.

Name of the compound (D.T.=diphenyl-thio-violurate)	Colour in the solid state	Remarks	Colour in solution (aqueous acetone)	M.P. (D)	Absorption Maxima A	Analysis (% S. Theo- retical with- in bracket)
Methylamine-D.T. ..	Deep olive-green	Glistening hexagonal prisms	Greenish-blue	128°	6010	8.72 (8.98)
Dimethylamine-D.T.	Brilliant green	Glistening hexagonal plates	Bluish emerald-green	185°	6030	8.43 (8.64)
Trimethylamine-D.T.	Olive-green	Glistening prisms	Bluish-green	123°	6015	8.30 (8.33)
Ethylamine-D.T. ..	Deep olive-green	Glistening needles	Deep olive-green	176°	6050	8.52 (8.64)
Diethylamine-D.T. ..	Brilliant green	Glistening hexagonal plates	Deep greenish-blue	128°	6070	8.00 (8.04)
Allylamine-D.T. ..	Greenish-grey	Glistening prismatic needles	Bluish-green	169°	6025	8.12 (8.37)
Isobutylamine-D.T. ..	Deep green	Do.	Indigo-blue	178°	6000	8.53 (8.04)
Isoamylamine-D.T. ..	Steel-grey	Do.	Deep blue	162°	6015	8.20 (7.76)
Quinoline-D.T. ..	Salmon-pink	Fine needles	Pale bluish-green	176°	5920	7.32 (7.04)
Piperidine-D.T. ..	Dull terra-cotta	Do.	Deep green	184°	6140	7.36 (7.80)
Isoquinoline-D.T. ..	Salmon-pink	Do.	Grass-green	174°	6009	7.37 (7.04)
Collidine-D.T. ..	Light mauve	Do.	Do.	186°	6010	7.57 (7.17)
Pyridine-D.T. ..	Bluish-green	Microscopic prisms	Yellowish-green	178°	5980	7.52 (7.92)
α -Picoline-D.T. ..	Dull terra-cotta	Prismatic needles	Sea-green	188°	5940	7.31 (7.65)
Lepidine-D.T. ..	Light bluish-green	Fine needles	Turquoise-blue	186°	6030	7.30 (6.83)
<i>o</i> -Toluidine-D.T. ..	Granite-grey	Prismatic needles	Dirty brownish green	180°	6025	7.95 (7.40)
Quinaldine-D.T. ..	Salmon-pink	Fine needles	Bluish-green	159°	6040	7.2 (6.83)
Phenetidine-D.T. (<i>p</i>)	Chocolate-brown	Prismatic needles	Dark olive-green	136°	6020	6.73 (6.92)
Anisidine-D.T. (<i>o</i>) ..	Greenish-grey	Rhombic prisms	Do.	128°	6000	7.54 (7.14)

TABLE II—(Contd.)

Name of the compound (D.T. = diphenyl-thio- violurate)	Colour in the solid state	Remarks	Colour in solution (aqueous acetone)	M.P. (D)	Absorption Maxima A	Analysis (% S. Theo- retical with- in bracket)
α -Naphthylamine- D.T.	Dirty brown	Glistening prismatic needles	Dirty brownish- green	161°	5860	6.92 (6.83)
<i>p</i> -Toluidine-D.T. ..	Reddish-brown	Prismatic needles	Grass-green	199°	6030	8.10 (7.40)
<i>m</i> -Toluidine-D.T. ..	Light oak- brown	Glistening hexa- gonal prisms	Greenish- brown	164°	6020	7.78 (7.40)
Brucine-D.T. ..	Bright bluish- green	Cubical crystals	Azure-blue	180°	6050	4.83 (4.45)
Potassium-D.T. ..	Deep emerald- green	Glistening rect- angular prisms	Brilliant green	219°	6560	8.84 (8.81)
Sodium-D.T. ..	Greenish-black	Do.	Intense emerald green	128°	6610	9.39 (9.22)
Ammonium-D.T. ..	Bluish-grey	Rectangular prisms	Greenish- blue	213°	6060	9.83 (9.35)
Quinine-D.T. ..	Light bluish- grey	Cubical crystals	Violet-blue	139°	5950	5.51 (4.90)
Veratrine-D.T. ..	Light greenish- grey	Do.	Moss-green	168°	6080	4.10 (3.49)
Cinchonidine-D.T. ..	Greyish-blue	Do.	Deep violet	140°	5970	5.32 (5.16)
Morphine-D.T. ..	Violet-black	Do.	Carmine- red	93°	5780	5.67 (5.24)
Thebain-D.T. ..	Dark grey	Do.	Brownish- red	123°	5825	4.83 (5.03)
Narcotin-D.T. ..	Greenish-grey	Do.	Reddish- brown	103°	5865	4.67 (4.33)

TABLE III.

Salts of Higher Homologues and Analogues of Diphenyl-thio-violuric Acid.

Name of the compound	Colour in the solid state	Remarks	Colour in solution (aqueous acetone)	M.P. (D)	Absorption Maxima $\overset{\circ}{\text{A}}$	Analysis (% S. Theoretical within bracket)
<i>(A) Acid-Di-o-tolyl-thio-violuric Acid.</i>						
Methylamine salt ..	Dark olive-green	Short hexagonal prisms	Deep olive-green	153°	6060	8.21 (8.33)
Diethylamine ,, ..	Bright bluish-green	Rhombic plates	Greenish-blue	181°	6190	7.84 (7.51)
Triethylamine ,, ..	Violet-grey	Small prismatic needles	Deep sage-green	155°	6400	7.32 (7.76)
Quinoline ,, ..	Light buff	Fine needles	Olive-green	212°	6075	7.11 (6.63)
Sodium ,, ..			Greenish-blue		6190	
<i>(B) Acid-Di-p-tolyl-thio-violuric Acid.</i>						
Methylamine salt ..	Light grey	Very fine needles	Brilliant blue-green	176°	6205	8.23 (8.33)
Diethylamine ,, ..	Bright bluish-green	Fine prismatic needles	Brilliant green	142°	6420	7.45 (7.52)
Trimethylamine ,, ..	Light dull blue	Fine needles	Do	164°	6425	7.18 (7.76)
Sodium ,, ..			Greenish-blue		6150	
<i>(C) Acid-Di-m-tolyl-thio-violuric Acid.</i>						
Methylamine salt ..	Light greenish-blue	Rectangular prisms	Dark olive-green	160°	6315 (6220)	8.21 (8.33)
Diethylamine ,, ..	Brilliant green	Glistening cubes	Deep indigo-blue	185°	6300 (6160)	7.84 (7.51)
Trimethylamine ,, ..	Greyish-blue	Do.	Deep violet	107°	5850	7.32 (7.76)
Quinoline ,, ..	Light buff	Fine needles	Light dirty green	177°	6005	6.97 (6.63)
Sodium ,, ..			Bluish-green		6235	

TABLE III—(Contd.)

Name of the compound	Colour in the solid state	Remarks	Colour in solution (aqueous acetone)	M.P. (D)	Absorption Maxima λ	Analysis (% S. Theoretical within bracket)
(D) <i>Acid-Di-m-xylyl-thio-violuric Acid.</i>						
Methylamine salt ..	Brownish-violet	Glistening rectangular prisms	Yellowish-green	148°	6035	7.35 (7.76)
Diethylamine ,, ..	Deep ash-grey	Cubic crystals	Bright green	104°	6165	7.52 (7.04)
Trimethylamine ,, ..	Dark violet-brown	Rectangular prisms	Greenish-blue	138°	6150	7.61 (7.27)
Sodium ,, ..			Brilliant green		6280	
(E) <i>Acid-Di-o-anisyl-thio-violuric-acid.</i>						
Methylamine salt ..	Medium grey	Rectangular prisms	Brilliant blue-green	151°	6170	7.54 (7.45)
Diethylamine ,, ..	Grey-blue	Rhombic prisms	Emerald green	154°	6265	7.38 (6.98)
Trimethylamine ,, ..	Violet-black	Rectangular prisms	Deep emerald green	105°	6280	7.36 (7.20)
Sodium ,, ..			Green		6150	
(F) <i>Acid-Di-p-phenetyl-thio-violuric acid.</i>						
Methylamine salt ..	Medium grey	Prismatic needles	Bluish emerald green	142°	6150	7.58 (7.20)
Diethylamine ,, ..	Greenish-grey	Cubical crystals	Emerald-green	136°	6350	6.43 (6.58)
Trimethylamine ,, ..	Greyish-green	Rectangular plates	Deep emerald green	114°	6410	6.32 (6.77)
Sodium ,, ..			Bluish green		6220	
Quinoline ,, ..	Leather-brown	Rhombic plates	Brown-red	136°	5980	6.41 (6.90)
(G) <i>Acid-Di-α-naphthyl-thio-violuric acid.</i>						
Methylamine salt ..	Dark brown	Rectangular plates	Brownish-red	147°	5960	7.42 (7.01)
Diethylamine ,, ..	Black	Prismatic needles	Do.	153°	5900	6.31 (6.42)
Trimethylamine ,, ..	Black	Glistening prismatic needles	Do.	112°	5860	7.04 (6.61)
Sodium ,, ..			Violet		5900	

TABLE IV.

Comparison of the Absorption Maxima of the Violurates, Thio-violurates and Diphenyl-thio-violurates.

Absorption Maxima.

Figures indicate wave-lengths in Angstrom units.

Salt of	With Violuric acid	With Thio-violuric acid	With Diphenyl-thio-violuric acid
Sodium	5830	5828	6610
Potassium	5830	5847	6560
Ammonium	5832	5837	6060
Methylamine	5782	5892	6010
Dimethylamine	5793	5858	6030
Trimethylamine	5712	5820	6015
Ethylamine	5697	5870	6050
Diethylamine	5699	5931	6070
Butylamine	5532	5850	6000
<i>o</i> -Toluidine	5626	5928	6025
<i>m</i> -Toluidine	5678	5941	6020
<i>p</i> -Toluidine	5684	5950	6030
α -naphthylamine	5499	5597	5860
Pyridine	5692	5886	5980
α -picoline	5692	5907	5940
Piperidine	5697	6023	6140
Quinoline	5683	5861	5920
Quinine	5537	5905	5950
Cinchonidine	5557	5927	5970
Brucine	5697	5975	6050

MICROPHOTOGRAPHS OF DIPHENYL-THIO-VIOLURIC ACID AND ITS
HIGHER HOMOLOGUES AND ANALOGUES



Diphenyl-thio-violuric acid



Di-*p*-tolyl-thio-violuric acid



Di-*m*-tolyl-thio-violuric acid



Di-*o*-tolyl-thio-violuric acid