

COLOUR IN RELATION TO CHEMICAL CONSTITUTION OF THE ORGANIC SALTS AND METALLIC DERIVATIVES OF ISONITROSO- DIPHENYL-THIOHYDANTOIN

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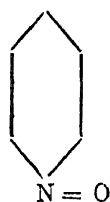
IN accordance with the "Theory of colour on the basis of molecular strain" advanced by Dutt,¹ the nitroso group is the most fruitful cause of intense colour amongst organic compounds on account of the high degree of molecular strain contained therein, as calculated from theoretical considerations. This is the reason why most of the well-known true nitroso compounds have very high absorption as can be seen from Table I.

TABLE I
Absorption Maxima of Nitroso Compounds

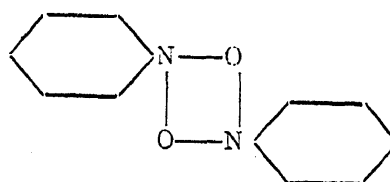
Nitroso compound	Absorption maxima (Å)	Colour in solution in alcohol
Nitrosobenzene	7300	Green
<i>p</i> -Nitrosotoluene	7300	Green
Nitrosomesitylene	7320	Dark green
Ter-nitrosobutane	6390	Blue
Ter-nitrosoisopropylacetone	6600	Dark greenish blue

On account of the high strain in the molecule, most of the nitroso compounds tend to lose their internal strain by formation of more or less stable bi- or trimolecular compounds. Thus the colourless and comparatively more stable nitrosobenzene in benzene solution is found to be bimolecular,

although in the vapour state it is intensely green, very unstable and monomolecular :

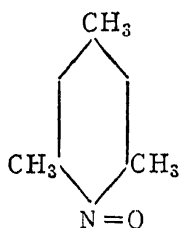


Nitrosobenzene
(Vapour; intense green)

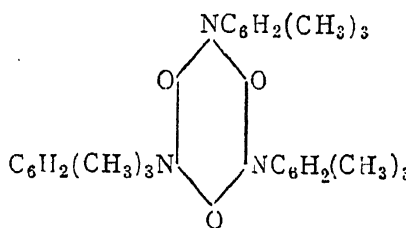


Nitrosobenzene
(Benzene solution; colourless)

Similarly the unstable nitrosomesitylene in alcohol solution and also in the vapour state is emerald green and monomolecular, but in benzene solution and also in the solid state it is colourless, perfectly stable and trimolecular :



Nitrosomesitylene
(In alcohol; emerald green)

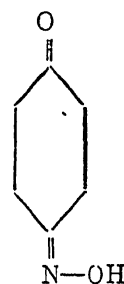


Nitrosomesitylene
(In benzene; colourless)

The internal strain of nitroso compounds is also lost by formation of isonitroso compounds whenever there is a possibility of isomerism by the migration of a hydrogen atom in vicinity, as in the cases of nitroso-phenols or nitroso-naphthols, which are generally only yellow in colour :

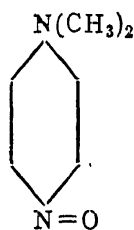


Nitrosophenol

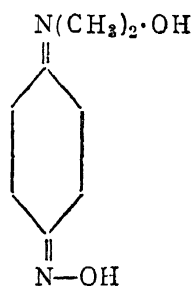
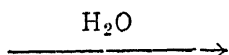


Quinoneoxime

Similar change also takes place by the action of water on nitrosodialkyl anilines. Thus nitroso-dimethyl aniline is dark green in colour in the solid state, but in aqueous solution it is only yellow in colour :



(Green)

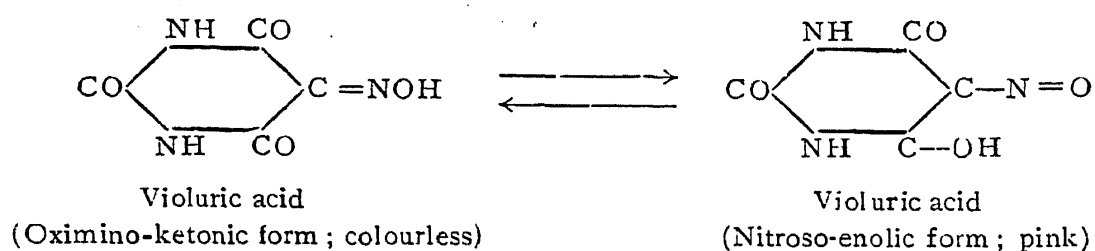


(Yellow)

Nitrosodimethylaniline

In many cases however there is a definite existence of resonance or tautomerism between the nitroso-enolic and the oximino-ketonic forms with a possibility of covalent links with chelate ring formations in the metallic derivatives such as in the cases of violuric acid and its various substituted derivatives and also in some of the isonitrosoisooxazolones studied by Dutt and his pupils, but all the interesting colour phenomena exhibited by these compounds can also be explained from the point of view of the theory of colour advanced by Dutt. This will be clear from the following explanations :

On account of the tautomerism between the nitroso-enolic and oximino-ketonic forms, many of the nitroso compounds do not exhibit the deep colours that are theoretically expected of them due to the extremely brief period during which they remain in the truly nitroso form. Thus in the classical example of violuric acid studied by Ghatak and Dutt,² the tautomerism between the two forms can be shown as given below :



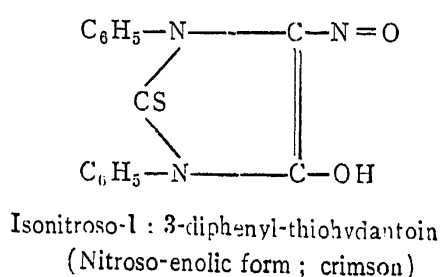
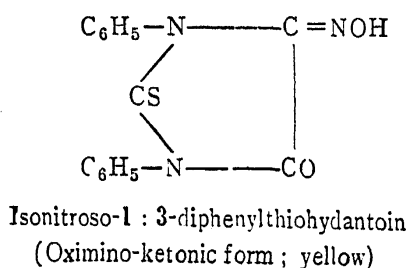
On account of this tautomerism, we find that violuric acid is colourless in the solid state and also in solution in non-hydroxylic solvents, and only pale pink in aqueous solution. But under special circumstances, that is, by the influence of organic or inorganic bases, the tautomerism between the two forms is arrested and the comparatively more acidic nitroso-enolic form is stabilised by salt formation. Consequently under such circumstances the deep colours that are expected of true nitroso compounds are developed. Thus we find that although violuric acid is colourless in the solid state and only very pale pink in aqueous solution, yet its salts with organic and inorganic bases are all crimson in colour, the intensity of the crimson coloration being roughly proportional to the strength of the basic character of the base undergoing salt formation. Exactly similar behaviour was noticed in the case of diphenyl-violuric acid by Prakash and Dutt,³ of thio-violuric acid by Lal and Dutt,⁴ of diphenylthio-violuric acid and its higher homologues and analogues by Dharam Dass and Dutt,⁵ of isonitroso-malonyl-guanidine by Dharam Dass and Dutt,⁶ of violantin and alloxantin by Gaiind and Dutt⁷ and of some derivatives of isonitroso-isooxazolones by Dutt and Dharam Dass,⁸ as given in Table II.

TABLE II
Colour of Isonitroso Compounds and their Salts

Name of the isonitroso compound	Colour of the substance	Colour of the salt
1 : 3-Diphenyl-violuric acid ..	Colourless	Purple
Thiovioluric acid	Light yellow	Purple
1 : 3-Diphenylthio-violuric acid ..	Light orange	Blue-green
Violantin	Colourless	Violet
Alloxantin	Colourless	Violet
Isonitroso-malonyl-guanidine ..	Light pink	Purple
Isonitroso-3-methyl-isooxazolone ..	Colourless	Crimson
Isonitroso-3-phenyl-isooxazolone ..	Colourless	Reddish-violet

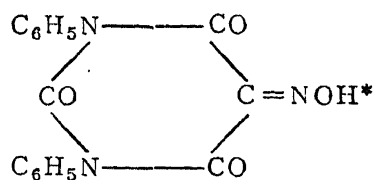
In all the above instances, the transformation of the colourless or weakly coloured isomer into the strongly coloured compound is produced by the addition of organic or inorganic bases, when in order to effect the neutralisation of the base the weakly acidic oximino-ketonic forms are converted into the strongly acidic nitroso-enolic forms, with consequent great intensification of colour due to the stabilisation of a true nitroso group in the molecular structure, and the more or less complete stoppage of resonance between the oximino-ketonic and nitroso-enolic forms.

In the present investigation, isonitroso-1 : 3-diphenyl-thiohydantoin, which has been prepared for the first time by the action of nitrous acid on 1 : 3-diphenyl-thiohydantoin which has the oximinoketonic configuration shown below, has been found to undergo similar type of transformation by the action of organic and inorganic bases with production of a nitroso-enolic structure, and consequent great intensification of colour. Thus :

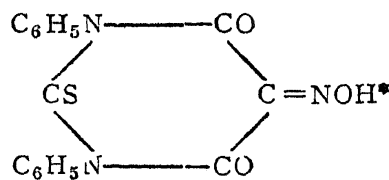


Isonitroso-1 : 3-diphenyl-thiohydantoin is bright yellow in the solid state and in solution in organic solvents (non-hydroxylic), but on the addition of alkali or organic bases, an intense crimson coloration is formed, recalling the behaviour of violuric acid. In hydroxylic solvents like alcohol and acetic acid, a pinkish-yellow coloration is formed, and in this respect also it is similar to violuric acid. The salts of the compound obtained with organic and inorganic bases are perfectly stable at the ordinary temperature, and in most of the cases are precipitated in a beautifully crystalline condition when an alcoholic solution of the substance is mixed with an alcoholic or aqueous solution of the base. Salts with the following bases have been obtained : potassium hydroxide, sodium hydroxide, ammonium hydroxide, methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, iso-butylamine, pyridine, piperidine, and nicotine. For the sake of abbreviation, the properties of these substances together with their absorption maxima have been given in Tables III and IV. As in the case of compounds described by previous workers, it has also been found in the case of the present substance, that in general the stronger basic character of the base undergoing salt formation, the greater is the intensity of the colour of the salt thus produced. Many of the salts formed, in the solid state are almost colourless or have only pale colours, but in solution in aqueous alcohol, the deep colours that are expected from their molecular configurations are more or less fully developed. With very weak bases like aniline or dimethylaniline, isonitroso-diphenylthiohydantoin does not produce any stable salt formation, and consequently in presence of these bases no intensification of colour occurs.

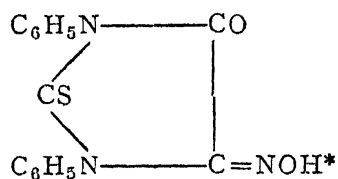
Compared to isonitroso-diphenylbarbituric acid (Prakash and Dutt³) and isonitroso-diphenylthio-barbituric acid (Lharam Dass and Dutt⁵), the intensification of colour of isonitroso-diphenylthio-hydantoin on salt formation is less pronounced, apparently due to the fact that in the first two compounds there are two CO groups in each of the molecules, capable of effecting the conversion of the isonitroso group into a true nitroso group by the transference of the labile hydrogen atom (marked with an asterisk), whereas in the third compound, there is only one such group existing. Consequently the possibility of formation of a true nitroso group with its concomitant intensification of colour is much greater in the first two cases than in the third. This is the reason why we find that the first two compounds form violet and green salts respectively, whereas the third form only crimson salts, although the molecular structures of all the three are closely analogous to one another. The idea will be quite clear by a look at the diagrams given below :



(IX) Isonitroso-diphenylbarbituric acid
(Violet salts)



(X) Isonitrosodiphenylthio-barbituric acid
(Green salts)



(XI) Isonitroso-diphenylthio-hydantoin (Crimson salts)

Experimental

Preparation of isonitroso-1 : 3-diphenylthio-hydantoin.—The 1 : 3-diphenylthio-hydantoin required for this purpose was prepared by the action of thio-carbanilide on monochloroacetic acid in an yield of about 64 per cent. in accordance with the method described by Lange.⁹ 20 grams of the substance dissolved in 250 c.c. of glacial acetic acid were treated with 60 grams of finely powdered sodium nitrite in six equal instalments with vigorous stirring, each instalment being added at the end of every 24 hours and the reaction mixture allowed to stand at the ordinary temperature during the intervals between the additions. At the end of a week, the reaction product was poured into a large excess of water, and the precipitated orange-yellow sticky substance separated from the aqueous mother-liquor by decantation. On allowing it to stand in contact with water for about 48 hours, the sticky material completely solidified to an orange-yellow crystalline mass (24.6 gm.), which was filtered off, washed with water, dried and extracted with xylene which removed a small quantity of a dark yellow, viscous, uncrystallisable material. The residue (21.8 gm.) after complete removal of the xylene by aeration, was fractionally crystallised a number of times from alcohol of decreasing concentration into three main fractions, namely :

Fraction 1.—A bright yellow substance (1.2 gm.) crystallising in small rhombohedra, melting at 245° C. This was found to be free from sulphur and on account of the small quantity available, its identity could not be established.

Fraction 2.—A pale cream-coloured substance (6.3 gm.) crystallising in fine prismatic needles melting at 176° C. and giving no coloration with alcoholic ammonia. This was identified to be unchanged 1 : 3-diphenylthio-hydantoin.

Fraction 3.—A bright yellow substance (11.6 gm.) crystallising in glistening rectangular prisms, melting sharp at 174° C., and giving an intense

crimson colour with alcoholic ammonia. This was identified to be isonitroso-diphenylthio-hydantoin.

Isonitroso-1 : 3-diphenylthio-hydantoin crystallises from 40 per cent. alcohol in bright yellow glistening rectangular prisms, and from ether or benzene, in long feathery needles, with silky lustre, and melting at 174° C. in either form. It is easily soluble in alcohol, acetone, ether, chloroform, benzene and glacial acetic acid, moderately soluble in toluene, xylene, carbon tetrachloride and petroleum ether and insoluble in water. The solutions of the substance in organic solvents are bright yellow, but on the addition of alkali or strong organic bases, crimson colours are developed which become slightly intensified by the addition of a trace of water.

Salts of isonitroso-1 : 3-diphenylthio-hydantoin.—These were prepared by taking the hydantoin in alcoholic solution and adding slightly more than the equimolecular proportion of the organic or inorganic base, also in alcoholic solution. In most of the cases the salt crystallised out spontaneously from the solution in a fine state, but in some of the cases the solution had to be evaporated very quickly to dryness with the aid of a blast from a table fan, and the resulting crystalline salt washed with a little dry ether in order to remove any excess of the base.

The salts thus formed are exceedingly fine crystalline substances which are easily soluble in most of the organic solvents with the exception of ether and petroleum ether in which they are very sparingly soluble. In water they are only slightly soluble, but in contact with that solvent, they undergo very rapid hydrolytic decomposition partially with regeneration of isonitroso-diphenylthio-hydantoin, and partly with formation of complex bye-products. The properties of isonitroso-1 : 3-diphenylthio-hydantoin and its salts are given in Table III.

Summary and Conclusion

1. Isonitroso-1 : 3-diphenylthio-hydantoin has been obtained for the first time by the action of nitrous acid on 1 : 3-diphenylthio-hydantoin.
2. Isonitroso-diphenylthio-hydantoin has a bright yellow colour in the solid state or in solution in organic solvents, but on treatment with alkalies or organic bases, intense crimson coloured salts are formed the transition of colour from yellow to crimson being sufficiently strong and sharp for the compound to act as an excellent indicator.
3. The change of colour of the above compound from yellow to crimson has been shown from theoretical considerations to be due to a fundamental

TABLE III
Properties of Isonitroso-1 : 3-Diphenylthio-Hydantoin and its Organic and Inorganic Salts

Salt with	Colour in the solid state	Remarks	Colour in aqueous solution	M.P. (°C.)	Absorption maxima (Å)	Analysis (% S, theoretical values in brackets)
Methylamine ..	Brownish pink	Rectangular plates ..	Dark crimson	129	5540	9.56 (9.75)
Dimethylamine ..	Bright pink	Rectangular plates and prisms	"	148	5520	9.31 (9.36)
Trimethylamine ..	Light buff	Long feathery needles ..	"	152	5480	8.81 (8.98)
Ethylamine ..	Yellowish pink	Rectangular plates ..	"	156	5520	9.22 (9.36)
Diethylamine ..	Bright pink	Long rectangular prisms	Crimson	179	5430	8.59 (8.65)
Triethylamine ..	Dark red	Rhombic prisms	Red	87	5270	8.15 (8.04)
Isobutylamine ..	"	Prismatic needles	"	167	5320	8.43 (8.65)
Pyridine ..	Light yellow	Glistening cubes ..	Orange	139	4550	8.29 (8.51)
Piperidine ..	Brownish pink	Long rectangular prisms	Dark crimson	158	5550	8.25 (8.37)
Nicotine ..	Pinkish brown	Rectangular plates ..	Red	132	5250	7.61 (6.98)
Potassium ..	Brownish pink	Glistening cubes ..	Dark crimson	167	5600	8.96 (8.55)
Sodium ..	Creamy yellow	Thin prismatic needles	"	188	5550	10.51 (10.10)
Ammonium ..	Bright yellow	Glistening cubes	"	112	5550	10.33 (10.20)
Free acid ..	"	Rectangular prisms ..	Yellow	174	4435	10.65 (10.77)

TABLE IV

Comparison of the Absorption Maxima of the Salts of Isonitroso-diphenyl-barbituric acid, Isonitroso-diphenylthio-barbituric acid and Isonitroso-diphenylthio-hydantoin

Figures indicate Wave-lengths in Angstrom Units

Salt of	With Isonitroso-diphenyl-barbituric acid	With Isonitroso-diphenylthio-barbituric acid	With Isonitroso-diphenylthio-hydantoin
Methylamine ..	5810	6010	5540
Dimethylamine ..	5805	6030	5520
Trimethylamine ..	5765	6015	5480
Ethylamine ..	5785	6050	5520
Diethylamine ..	5875	6070	5430
Isobutylamine ..	5870	6000	5320
Pyridine	5825	5980	4550
Piperidine	5670	6140	5550
Nicotine	5650	..	5250
Sodium	5835	6610	5550
Potassium	5840	5660	5600
Ammonium	5845	6060	5550

change in the constitution of the molecules from an oximinoketonic to a nitroso-enolic form.

4. The above change is quite in accordance with a "Theory of colour on the basis of molecular strain," advanced by Dutt.

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