

yellow solid separated and was recrystallized from methyl alcohol (160 cc. per g.); yield 43%. The yellow needles had m. p. 192–193° slight dec.

*Anal.* Calcd. for  $C_{21}H_{18}N_2$ : C, 84.50; H, 6.08; N, 9.40. Found: C, 83.84; H, 6.10; N, 9.29.

[1,2 - Dimethylindole - (3)] - [1 - methylquinoline-(4)]-dimethine-cyanine Iodide (XII).—(a) Lepidine methiodide (1.43 g., 1 mol) was condensed with 1,2-dimethyl-3-indolealdehyde (0.86 g., 1 mol) by refluxing in acetic anhydride (15 cc.) for three minutes. Dye separated from the hot mixture; yield 68%. After recrystallization from methyl alcohol (230 cc. per g.) the dye formed dull brownish crystals with m. p. 297–298° dec.; yield 59%.

*Anal.* Calcd. for  $C_{22}H_{21}N_2$ : I, 28.83. Found: I, 28.82.

(b) The dye was obtained when the base X (0.5 g., 1 mol) was heated on a steam-bath to refluxing with methyl iodide (2 g., 8 mols) in nitrobenzene (10 cc.) for two hours; yield 88%. Found: I, 28.88 after recrystallization.

(c) XII was similarly obtained from XI; yield 81%. Found: I, 28.95 after recrystallization. The identity of the specimens from a, b and c was established by m. p. and mixed m. p. determinations and by absorptions.

### Summary

A number of cyanine dyes have been compared with respect to absorption with the bases derived from them by removal of the elements of alkyl halide. In most cases the bases are lighter in color than the corresponding cyanines, but this is not invariably the case. These facts may be explained on the basis of the resonance theory. Certain of the arguments used have been confirmed by dipole moment determinations.

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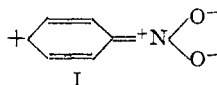
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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

## The Steric Inhibition of Resonance in Aromatic Nitro Compounds<sup>1</sup>

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From a study of dipole moments, Birtles and Hampson have concluded<sup>1b</sup> that, in the aromatic nitro compounds, the resonance with quinoid structures of the type I<sup>2</sup> is sterically inhibited



when the nitro group lies between methyl groups in the two ortho positions. The work described in the present paper was undertaken in order to obtain chemical evidence bearing upon this hypothesis.<sup>3</sup>

The particular problem investigated was that presented by the striking effect of para nitro groups upon the acid strengths of the phenylmethanes. While triphenylmethane has been assigned<sup>4</sup> a  $pK$  value greater than 33, its trinitro

derivative, 4,4',4''-trinitrotriphenylmethane (hereafter called simply trinitrotriphenylmethane) is sufficiently acidic for its salts to be stable in aqueous alcohol.<sup>5</sup> It seems probable that resonance of the sort considered is at any rate partially responsible for this greater acidity of the trinitro derivative, since the quinoid structures increase the positive electrostatic potential at the position of the ionizable hydrogen atom, and since, moreover, the negative ion can be stabilized by resonance with these quinoid structures to a greater extent than the undissociated molecule.

If the above reasoning is correct, and if the contention of Birtles and Hampson is justified, it follows that 3,3',3'',5,5',5''-hexamethyl-4,4',4''-trinitrotriphenylmethane (hereafter called simply trinitrotrixylylmethane) should be appreciably less acidic than trinitrotriphenylmethane. The former compound was, accordingly, prepared, and its acid strength was investigated in a manner analogous to that employed by Conant and Wheland<sup>6</sup> and by McEwen.<sup>4</sup> The sodium salts of both trinitrotriphenylmethane and trinitrotrixylylmethane are characterized by intense purple colors, and, consequently, the position of the equilibrium between either methane and its salt can be estimated colorimetrically. Since

(1) Abstract of a thesis presented by A. A. Danish to the faculty of the Division of the Physical Sciences of the University of Chicago in partial fulfillment of the requirements for the degree of Master of Science, December, 1938.

(1a) Present address: VioBin Corporation, Chicago, Illinois.

(1b) R. H. Birtles and G. C. Hampson, *J. Chem. Soc.*, 10 (1937), see also C. E. Ingham and G. C. Hampson, *ibid.*, 981 (1939).

(2) L. E. Sutton, *Proc. Roy. Soc. (London)*, **A133**, 668 (1931); *Trans. Faraday Soc.*, **30**, 789 (1934).

(3) Since the present research was started, several papers have appeared dealing with the steric inhibition of resonance from the chemical point of view. These have provided strong support for the existence of such an effect in various types of compounds, but apparently little work of this sort has been done with nitro compounds. See for example, W. G. Brown, A. H. Widiger and N. J. Letang, *THIS JOURNAL*, **61**, 2597 (1939); G. Baddeley, *Nature*, **144**, 444 (1939).

(4) W. K. McEwen, *THIS JOURNAL*, **58**, 1124 (1936).

(5) V. v. Richter, *Ber.*, **21**, 2475 (1888).

(6) J. B. Conant and G. W. Wheland, *THIS JOURNAL*, **54**, 1212 (1932).

only qualitative results were desired, no attempt was made to put the experiments upon a quantitative basis or to determine the values of the dissociation constants. It was considered sufficient to establish the relative stabilities of the two salts in a series of weakly acidic solvents.

The results of the experiments can be summarized as follows. The sodium salt of trinitrotrixylmethane is stable in acetophenone and aniline, and in cyclohexylamine containing up to about 15% of methyl alcohol or 30% of ethyl alcohol; it is solvolyzed completely in methyl alcohol, ethyl alcohol and water-dioxane mixtures. The sodium salt of trinitrotriphenylmethane, on the other hand, is stable in all of the solvents named but is decomposed by phenol. Thus, it is evident that trinitrotrixylmethane is a weaker acid than trinitrotriphenylmethane by several  $pK$  units. This conclusion is consistent with, and lends support to, the theory of Birtles and Hampson. However, since the observed difference in acidity is apparently not very great, the evidence is insufficient to establish the theory beyond question.<sup>7</sup> The problem is being investigated further.

### Experimental. I

All melting points given below are uncorrected.

**3,3',3'',5,5',5''-Hexamethyl Triphenylmethyl Chloride.**—*sym*-Bromoxylene<sup>8</sup> was transformed into the Grignard reagent and treated with ethyl chlorocarbonate in the usual way. The resulting trixylylcarbinol was not purified but was transformed directly into the corresponding trixylylmethyl chloride by the action of dry hydrogen chloride in absolute ether.<sup>9</sup> The yield of crude chloride was 46%, based upon the amount of bromoxylene used. A small portion, after crystallization from high-boiling ligroin saturated with dry hydrogen chloride, formed colorless needles melting at 210°.

*Anal.* Calcd. for  $C_{26}H_{27}Cl$ : Cl, 9.77. Found: Cl, 9.83.

**3,3',3'',5,5',5''-Hexamethyltriphenylmethane.**—The crude trixylylmethyl chloride was reduced<sup>10</sup> with zinc dust in acetic acid solution under an atmosphere of carbon dioxide, and the resulting trixylylmethane was purified by crystallization from alcohol and water. The yield was 72% of the theoretical, based upon the amount of crude chloride used. The pure methane was colorless and melted at 108°.

*Anal.* Calcd. for  $C_{26}H_{28}$ : C, 91.41; H, 8.59; mol. wt., 328.2. Found: C, 91.52; H, 8.43; mol. wt. (camphor), 310.

(7) The correction for the direct inductive effect of the methyl groups is probably not significant, because the effect of the analogously situated methyl group in *m*-cresol upon the acidity of the substance appears to be quite small; cf. D. R. Boyd, *J. Chem. Soc.*, **107**, 1538 (1915).

(8) E. Fischer and A. Windaus, *Ber.*, **38**, 1967 (1900).

(9) M. Gomberg, *ibid.*, **35**, 2401 (1902).

(10) M. Gomberg, *ibid.*, **36**, 383 (1903).

**3,3',3'',5,5',5''-Hexamethyl - 4,4',4''-trinitro - triphenylmethane.**<sup>11</sup>—The trixylylmethane prepared as above was nitrated with fuming nitric acid in a mixture of acetic acid and acetic anhydride in accordance with the method given by Powell and Johnson<sup>12</sup> for the nitration of mesitylene. After the completion of the reaction, the mixture was poured into an excess of ice water. The product, which then precipitated, was separated from the aqueous solution and washed free of acid. After one crystallization from glacial acetic acid and two from alcohol, the trinitrotrixylmethane melted at 247°. The yield was only 16% of the theoretical. An attempt to obtain further material by adding water to the mother liquor from the original crystallization provided only a reddish oil, which changed to a resinous solid after a few hours of standing, and the composition of which could not be determined.

*Anal.* Calcd. for  $C_{23}H_{25}N_3O_6$ : N, 9.07; mol. wt., 463. Found: N, 9.06; mol. wt. (camphor), 465.

**3,3',3'',5,5',5''-Hexamethyl - 4,4',4''-triaminotriphenylmethane by Reduction of the Nitro Compound.**—The trinitrotrixylmethane was reduced with zinc dust in boiling glacial acetic acid.<sup>13</sup> The product, obtained in 64% yield after crystallization from dioxane and water, had no definite melting point. It darkened at 190° and decomposed completely at 275–280°.

*Anal.* Calcd. for  $C_{23}H_{31}N_3$ : N, 11.25. Found: N, 11.11.

**3,3',3'',5,5',5''-Hexamethyl - 4,4',4''-triaminotriphenylmethane by the Method of Giacalone.**<sup>14</sup>—This preparation, which was undertaken in order to obtain material for comparison with that prepared as above, proceeded in two steps. First, 2,2',2'',6,6',6''-hexamethyltrianilidomethane was made by condensation of 2-amino-*m*-xylene with ethyl orthoformate, and then this was rearranged to the triaminotrixylylmethane. The reactions went much less readily than those reported by Giacalone, and more vigorous conditions were necessary.

(a) Forty-five grams of the xylylene and 30 g. of the ortho ester were refluxed together for twenty-four hours. From the resulting mixture, there was obtained 7 g. of the trianilido compound, melting at 179° (from benzene).

*Anal.* Calcd. for  $C_{23}H_{31}N_3$ : N, 11.25. Found: N, 11.26.

(b) One and one-half grams of the above trianilido compound, 3 g. of 2-amino-*m*-xylene, and 3 g. of 2-amino-*m*-xylene hydrochloride were heated together in an oil-bath at 170–175° for forty-eight hours and then at 140° for an additional fifty-three hours. The resulting mixture was steam distilled until no more volatile matter came over. From the residue in the flask was obtained 0.052 g. of the triaminotrixylylmethane. No unreacted starting material could be recovered, since extensive decomposition had occurred. In two preliminary runs, in which the heating was continued for only twenty-five and forty-two hours, respectively, the starting materials were recovered

(11) The proof that the three nitro groups occupy the 4,4',4'' positions is given later.

(12) W. W. Hartman, "Organic Syntheses," Vol. XIV, John Wiley and Sons, Inc., N. Y., 1934, p. 68.

(13) J. B. Shoesmith, C. E. Sosson and A. C. Hetherington, *J. Chem. Soc.*, 2221 (1927).

(14) A. Giacalone, *Gazz. chim. ital.*, **62**, 577 (1932).

unchanged, but no rearrangement product was obtained. The triaminotrixylylmethane, after crystallization from dioxane, darkened at 190° and decomposed completely at 275–280°.

*Anal.* Calcd. for  $C_{23}H_{21}N_3$ : N, 11.25. Found: N, 11.04.

**Comparison of the Samples of 3,3',3'',5,5',5''-Hexamethyl-4,4',4''-triaminotriphenylmethane from the Two Sources.**—The two samples of triaminotrixylylmethane, prepared, respectively, by the reduction of the corresponding trinitro compound and by the method of Giacalone, exhibited the same behavior on melting, as did also a mixture of the two. This evidence of their identity was not conclusive, however, since the substances had merely decomposition points and not true melting points. A crystallographic comparison was accordingly made,<sup>15</sup> and this showed the two to be identical.

The fact that the same substance was obtained by the two methods establishes its structure; the preparation from the trinitro compound shows that it is a derivative of 3,3',3'',5,5',5''-hexamethyltriphenylmethane, and the preparation from 2-amino-*m*-xylene shows that each amino group lies between two methyl groups in one of the benzene rings. Thus, the substance can only be 3,3',3'',5,5',5''-hexamethyltriphenylmethane. The proof of the structure of the corresponding trinitro compound now follows at once.

## II

The solvents used in the following tests were purified as stated.

Water: distilled water was used.

Methyl and ethyl alcohols: the commercial absolute alcohols were distilled over magnesium methoxide and ethoxide, respectively.

Acetophenone, aniline, cyclohexylamine, and dioxane: the Eastman Kodak Co. products were distilled and fractions boiling over a 1° range were retained. The dioxane was kept over sodium.

Some difficulty was encountered at the outset in devising an experimental procedure for the comparison of acid strengths, and many of the preliminary results were neither reproducible nor consistent. The procedures described below, however, were entirely satisfactory. All the tests were made as rapidly as possible, since the colors were discharged in a few minutes as a result of oxidation by the air.

**Water as Solvent.**—To approximately 1 mg. of trinitrotriphenylmethane dissolved in 1/4 g. of dioxane was added slowly 10 cc. of a 1 *N* solution of sodium hydroxide in water. The intense bluish-purple color of the salt appeared immediately with the first few drops of the aqueous solution. The color became fainter and more reddish as the remainder of the base was added, but it was still distinctly perceptible even after dilution of the solution with a further 10 cc. of water. The fading of the color presumably was due to the decreasing solubility of the methane, which precipitated from the solution.

When this experiment was carried out with trinitrotrixylylmethane, the color of the corresponding salt was not perceptible at any time.

**Methyl or Ethyl Alcohol as Solvent.**—When trinitrotriphenylmethane was added to a methyl alcoholic solution of sodium methoxide, or to an ethyl alcoholic solution of sodium ethoxide, the intense purple color of the salt was formed immediately. The concentrations used were not critical. If the solutions were diluted with water, the color persisted as long as an appreciable quantity of the methane remained dissolved, but if an excess of phenol were added, the color was discharged immediately.

Approximately 1 mg. of trinitrotrixylylmethane was dissolved in 5 g. of the alcohol in question, and a solution of the corresponding sodium alkoxide was prepared from 0.5 g. of sodium and 10 g. of the alcohol. When 1 cc. of each of these two solutions were mixed, no color appeared in either the methyl or the ethyl alcoholic solution. Cyclohexylamine was now added slowly. The color of the salt became just perceptible after the addition of about 10 cc. of cyclohexylamine to the methyl alcoholic solution, or of about 4 cc. to the ethyl alcoholic solution.

**Cyclohexylamine as Solvent.**—A dilute solution of sodium cyclohexylamide in cyclohexylamine was prepared by the action of sodium upon a large excess of the amine in the presence of naphthalene.<sup>16</sup> The concentration of the amide solution was not critical. When about 1 mg. of either trinitrotriphenylmethane or trinitrotrixylylmethane was added to 2–4 cc. of the solution, the intense purple color of the corresponding salt developed immediately.

**Acetophenone or Aniline as Solvent.**—A small amount of the solution of sodium cyclohexylamide in cyclohexylamine, prepared as above, was added to a larger quantity of acetophenone or aniline. The addition of about 1 mg. of either of the two methanes to 2–4 cc. of the resulting solution again produced immediately the color of the salt. The color was not discharged on the addition of further quantities of acetophenone or aniline, as the case might be, although it did become less intense as a result of dilution.

The authors wish to express their appreciation to Mr. Kurt Eder for making the elementary analyses reported in this paper, to Mr. George Monk, Jr., for carrying out the crystallographic comparison, and to Mr. R. D. Kleene for helping with some of the preliminary experiments upon the trinitrotrixylylmethane.

## Summary

In order to obtain evidence bearing upon the hypothesis of Birtles and Hampson that methyl groups in the two ortho positions can inhibit the resonance of a nitro group with an aromatic ring, 3,3',3'',5,5',5''-hexamethyl-4,4',4''-trinitrotriphenylmethane has been prepared and its acid strength compared with that of the corresponding trinitrotriphenylmethane. It was found, in agreement with the hypothesis of Birtles and Hampson, that the former substance is somewhat less acidic than the latter.

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(15) By Mr. George Monk, Jr.

(16) K. Ziegler, *Chem. Abs.*, **29**, 6250 (1935).