A SPECTROCHEMICAL STUDY ON THE CHEMICAL CONSTITUTION OF A REACTION PRODUCT BETWEEN CENTRALITE AND GASEOUS NITROGEN PEROXIDE. DINITRODIPHENYLETHYLUREA.

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Diphenyl-diethyl-urea, known as "CENTRALITE" (C/L), is used in several countries as a good gelatinizer or stabiliser for the smokeless powders and is now investigated in many explosives laboratories in the world. The great stabilizing effect of this substance is no doubt due to reaction of it with formation of stable nitrocompounds, preventing the injurious action of NO_2 gas and its acids produced by the spontaneous decomposition of nitroglycerine and nitrocellulose. From the stability point of view, it is an interesting and important problem, to see whether tetranitrocentralite is formed or not by the reaction between centralite and NO_2 gas at room temperature. In the Note,⑴ published in 1926, M. A. Apard reported on the formation of tetranitrocentralite which was obtained in a very small quantity as deep yellow powder by crystalizing the residue, produced with extraction by benzene solution, with ethyl alcohol. It is, however, doubtful whether the yellow powder is really tetranitrocentralite or not, because of the very small quantity. The author carried out the reaction between NO_2 gas and powdered centralite almost in the same manner, the time of the reaction being a little longer, and was able to separate a small quantity of yellow powder from a dark reddish, syrupy mass of the reaction product by treating with benzene. This powder crystallized from acetone as minute thin plates, melting at 207–210°C., somewhat different from the melting point (175°C.) of tetranitrocentralite.

The author started to study the absorption spectra of centralite, dinitrocentralite, tetranitrocentralite and the sample in question. The following figure shows a comparison of the absorption curves. Optical behaviours of the unknown compound resemble to that of dinitrocentralite, the absorption maximum of which is observed at 3200Å, while that of the former at 3350Å. On the other hand, the tetranitrocentralite is found to show no selective absorption. The small difference between absorption spectra of the unknown substance and dinitro-

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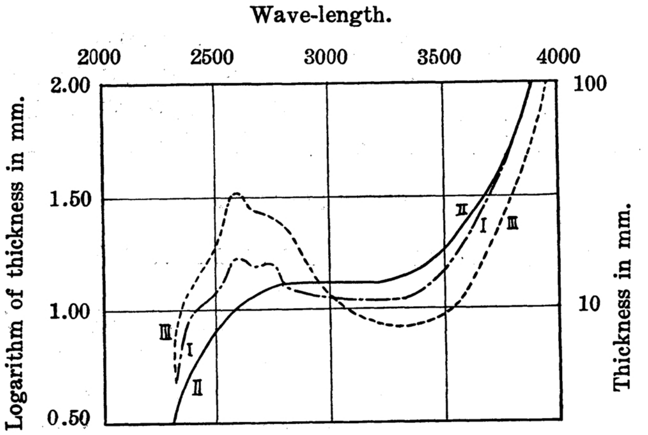
(1) *Mém. Poudres*, **22** (1926), 181.



I. Dinitrodiphenyldiethylurea (0.0001% Alcoholic solution).
II. Tetranitrodiphenyldiethylurea („).
III. Unknown substance („).

Fig. 1.

centralite has been investigated position and number of nitrogroups.

Nitrogen content in the unknown substance determined by micro-analysis (micro-duma.) is given below.

Subst. = 2.20 mg.; N_2 = 0.319 c.c. at 26.0°C and 759 mm. Found: N = 16.6%.

The relation between number of nitrogroups and nitrogen percentages in nitro-compounds of centralite is shown in the following table.

	mono.	di.	tri.	tetra.
N%	13.59	15.63	17.81	18.75

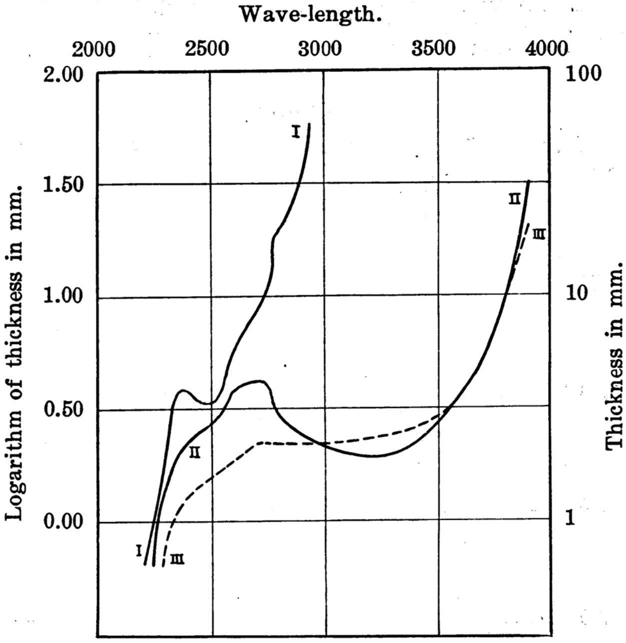
Thus the new substance can hardly be expected to be other than dinitro- or trinitro-derivative. The position of nitrogroup in a benzene ring accompanied with an acylimide group is, as a rule, ortho- or more likely para-position in the reaction at ordinary temperatures. In the case of the nitration of centralite and also in the reaction between NO_2 gas and centralite, the easiest product is sym.-*p*-dinitrocentralite; and then, with regard to the structure of the compound in question, all possible cases of di- and tri-nitrocentralites, except meta-structures and extremely unsymmetrical nitrocompounds which are improbable, are only the following.

(1) 4-4′-dinitro C/L. (Paraposition in a nucleus).
(2) 2-2′-dinitro C/L., 2-6-2′-trinitro C/L. (Orthposition in a nucleus).
(3) 2-4-4′-trinitro C/L., 2-4-2′-trinitro C/L. (Ortho- and para-position in a nucleus).

A relationship between these chemical constitutions and absorption curves has been studied. Intensity of the absorption band in the case of ortho-compound is feebler and the form is not simple compared with para-compound as Figs. 4 and 5 show, while the unknown compound in question has simply a deep and wide absorption band. From this point, it is not possible to consider that it should be ortho-compound as the 2nd.

The hypochromic influence of two or three nitrogroups takes mutually metaposition from the same optical behaviours of 2-4-2′-4′-tetranitrocentralite (Fig. 2), 2-4-dinitrophenylurethane (Fig. 3), 2-4-6-trinitrobenzene,⑴ and 2-4-6-trinitroacetanilide (Fig. 4), so that the compound is not the 3rd type. There remains only the structure of the 1st type, in which each nitrogroup takes para-position for acylimide groups from the position of absorption band and its extinction coefficient, although it is not 4-4′-dinitrocentralite.

As for light absorption some para-nitro aromatic compounds with

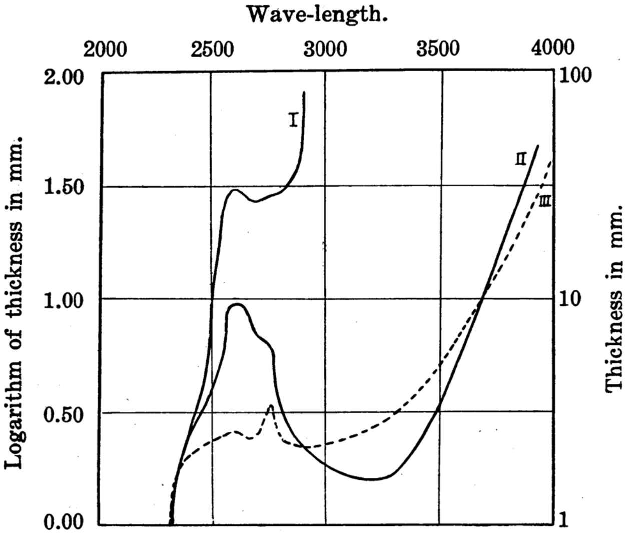


I. Diphenyldiethylurea (0.001 mol. in alcohol).
II. *p*-Nitrodiphenyldiethylurea (,,).
III. 2-4-2′-4′-Tetranitrodiphenyldiethylurea (,,).

Fig. 2.

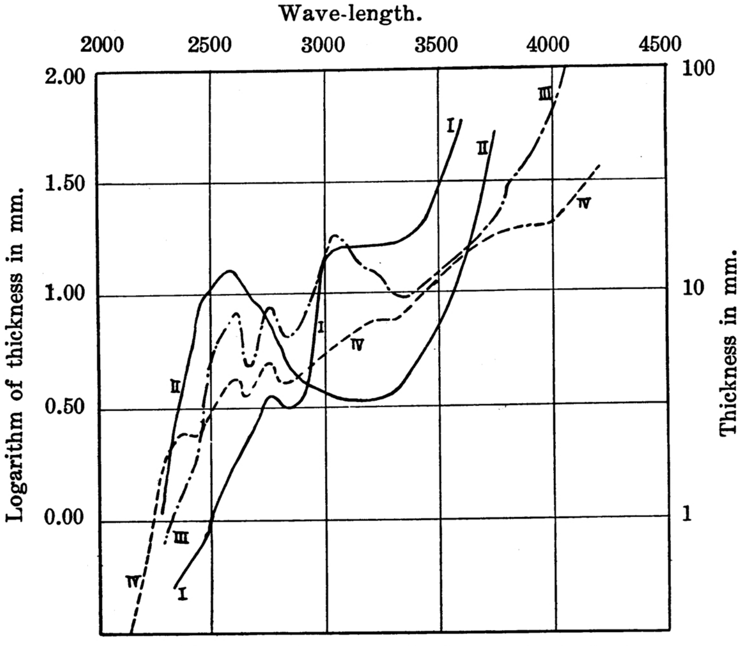
⑴ *J. Chem. Soc.*, **103** (1913), 2085. *Ber.* **42** (1909), 2119; **43** (1910), 1662; **52** (1919), 493.

Fig. 3.



I. Phenylurethane (0.001 mol. in alcohol).
II. p-Nitrophenylurethane (,,).
III. 2-4-Dinitrophenylurethane (,,).

Fig. 4.



I. m-Nitracetanilide (0.001 mol. in alcohol).
II. p-Nitracetanilide (,,).
III. o-Nitracetranilide (,,).
IV. 2-4-6-Trinitracetanilide (,,).

acylimide group are found to be almost the same as the following table shows.

	Wave length	log ε.
p-Nitroacetanilide	320 m. μ.	ca. 3.5
p-Nitrophenylurethane	320 ,,	,, 3.8
Sym.-*p*-dinitro C/L	325 ,,	,, 3.8
Unknown compound	335 ,,	,, 3.8

These facts indicate that its formula is of a paranitro structure, and only small difference between unknown compound and dinitro C/L, which has more hypochromic influence than the former, may not be the influence of nitrogroup, but that of C_2H_5-group when compared with *p*-nitroacetanilide and *p*-nitroethylacetanilide (Fig. 5). From the above considerations, the unknown compound might be dinitrodiphenylethylurea or dinitrodiphenyl-urea, one or two of ethyl-groups being expelled from dinitrocentralite. Checks and determinations have been carried out by measurements of molecular weight and microanalysis of elements in the constituents. By Rast's method, the following results have been obtained.

Camphor	Sample	Temp. depres.	Mol. wt.
0.0924 gr.	0.0044 gr.	7.6°C.	3.1×10^2
0.0889 gr.	0.0053 gr.	9.9°C.	3.0×10^2

These values being less than those of dinitrocentralite, the structure of which, excluding ethyl-group, is also probable, and there remains two cases as given below.

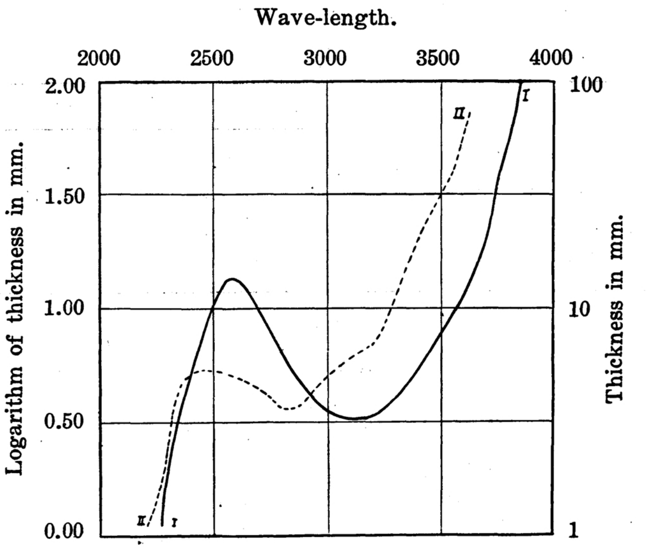
	Mol. wt.
Dinitrodiphenylethylurea	330
Dinitrodiphenylurea	302

The percentages of the elements of these compounds are the following.

Calc. for	C	H	N	O
Dinitrodiphenylethylurea ($C_{15}H_{14}N_4O_5$)	54.6	4.24	17.0	24.2
Dinitrodiphenylurea ($C_{13}H_{10}N_4O_5$)	51.6	3.32	18.5	26.5

The result of the analysis of the sample is given below.

Anal.: Subst. = 4.54; CO_2 = 9.05; H_2O = 1.98 mg.
Found: C = 54.3; H = 4.8; N = 16.6 %.



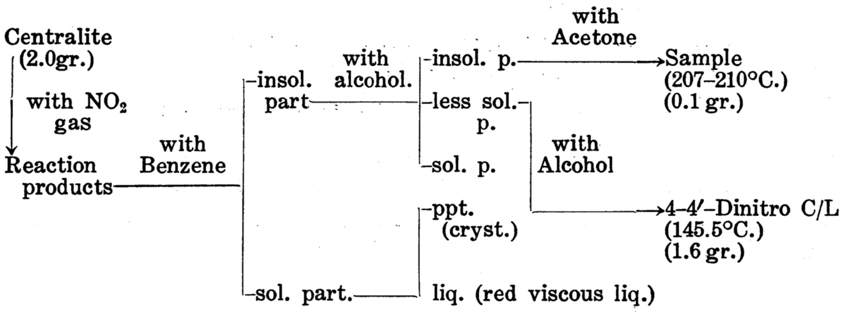
I. *p*-Nitracetanilide (0.001 mol. in alcohol).
II. *p*-Nitroethylacetanilide („).

Fig. 5.

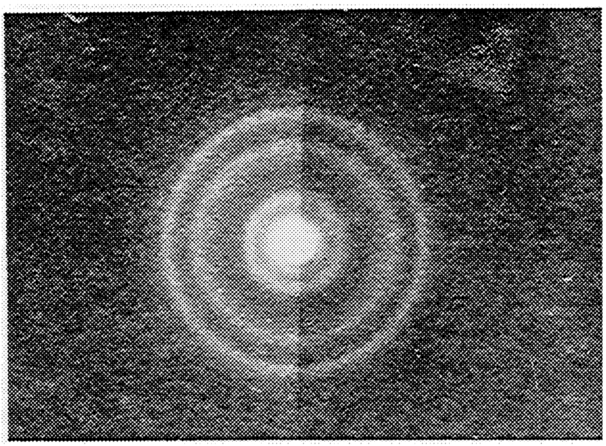
These are quite coincident with that of dinitrodiphenylethylurea. By these results and identification of that obtained by the synthesis which will be described later, the high melting point compound from centralite has been proved to be the dinitrodiphenyl-ethyl-urea.

Experimental Part.

Formation and Separation of the Sample. When NO_2 gas, diluted with air, was introduced in a bottle, containing 2.0 gr. of powdered centralite, the latter readily converted, from surface inward, into a viscous liquid of dark greenish colour, which turned brownish after allowing to stand overnight. This operation was repeated throughout a month or so, until no more reddish brown gas of NO_2, remained unchanged, and the viscous liquid partially solidified. On the mass of the products, the fractional separation was carried out with benzene, then with alcohol, and 5% of the sample (0.1 gr.) was obtained from the insoluble part in benzene and the other part was almost dinitrocentralite that was 80% corresponding to the initial substance. The process of the separation is given in the following table.



Sample obtained from the part insoluble in benzene and in alcohol, crystallized from acetone solution, consisted of yellow very thin plate crystals melting at 207–210°C., while that obtained from alcohol was faintly greenish yellow powder before recrystallisation. It is hardly soluble in ordinary solvents, especially in benzene, slightly soluble in small amount in acetic acid and acetone. The X-ray photograph obtained by Debye's method is shown in the following figure.



X-ray photo. of unknown subs. × 0.7
(Anticathode: Cu. dist. = 50 mm.)

Fig. 6.

4-4′-Dinitro-diphenyl-ethylurea. This substance was prepared by nitration of ethyldiphenylurea, which was obtained from phenylethylureachloride and aniline, at the temperature not exceeding 15°C. Twice recrystallisations with acetone suffice to render the raw product quite pure as crystals melting at 213.2–213.5°C.

Anal.: Subst. = 7.353; CO_2 = 14.62; H_2O = 3.26 mg.
Subst. = 1.921 mg.; N_2 = 0.287 c.c. at 23.0°C. and 775.3 m.m.
Found: C = 54.3; H = 4.9; N = 16.9%.
Calc. for $C_{15}H_{14}N_4O_5$: C = 54.6; H = 4.2; N = 16.9%.

Properties.—Very thin plate of yellow colour, insoluble or hardly soluble in ordinary solvents, only soluble in hot acetone. The absorption maximum was observed at 335 m.μ. Both in the absorption spectrum and X-ray photograph, the substance bears excellent resemblence to the sample obtained from C/L.

4-4′-Dinitrodiphenyldiethylurea. Centralite dissolved in glacial acetic acid was nitrated with nitric acid (sp. gr. 1.4) at a temperature not exceeding 15°C. and the product was crystallized from glacial acetic acid, then recrystallized from alcohol (M.P. 145.5°C.). In 0.001 mol alcoholic solution, the absorption maximum was observed at 325 m.μ.

2-4-2′-4′-Tetranitrodiphenyldiethylurea. This substance was obtained by nitration of centralite by conc. nitric acid (sp. gr. 1.5) at about 10°C. The product was crystallized from glacial acetic acid (M.P. 175°C.). In the 0.001 mol alcoholic solution, no absorption band was observed except an inflection in the absorption curve (Fig. 2).

Phenylurethane. The sample was prepared from aniline and diethylcarbonate which was obtained by the reaction between ethylalcohol and phosgene, $COCl_2$. The product melted at 51.5°C. The absorption maximum was observed at 269 m.μ. (Fig. 3).

***p*-Nitrophenylurethane.**(1) By introducing nitric acid into etheric solution of phenylurethane, the sample was prepared (M.P. 127°C.), the absorption maximum of which was observed at 325 m.μ. (Fig. 3).

2-4-Dinitrophenylurethane.(2) This substance was prepared by dissolution of phenylurethane in nitric acid (D. 1.5) at low temperature (M.P. 110–111°C.). In its absorption curve only slight maxima were observed at 268 m.μ. and 288 m.μ. (Fig. 3).

***o*-Nitracetanilide. *m*-Nitracetanilide.** Both nitracetanilides were prepared from *o*-nitraniline(3) or *m*-nitraniline(4) and acethylchloride at ordinary temperature. The former melts at 92–93°C., and the latter

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(1) *Ann.*, **233**, 9.
(2) *Rec. trav. chim.*, **10**, 141.
(3) *Ber.*, **39** (1906), 3903.
(4) *Ann.*, **57** (1846), 217.

at 145°C. These substances showed the following absorption maxima.

o-nitracetanilide	266 m.μ.	283 m.μ.	333 m.μ.
p-nitracetanilide		284 m.μ.	332 m.μ.

p-Nitracetanilide.(1) **p-Nitroethylacetanilide.**(2) By nitration of acetanilides, these two samples were obtained, the former melting at 207°C., the latter at 117–118°C. They show each a wide absorption band, the maximum of the former being observed at 321 m.μ., while that of the latter at 285 m.μ. (Fig. 5).

2-4-6-Trinitroacetanilide.(3) The substance was prepared from picramide and acetylchloride. It decomposed at 208–211°C.

Anal.: Subst. = 3.950 mg.; N_2 = 0.704 c.c. at 24.0°C and 766.1 m.m.

Found: N = 20.60 %. Calc. for $C_7H_6N_4O_7$: N = 20.68 %.

In its absorption curve four slight maxima were observed at 243 m.μ., 265 m.μ., 283 m.μ. and 311 m.μ. Three nitrogroups mutually in meta-positions in a benzene ring shows the hypochromic influence (Fig. 4).

In conclusion, the author wishes to express his gratitude to Prof. Y. Shibata for his suggestions and advice in connection with the spectrochemical part, to Prof. N. Yamaga for his interest in this work and to Mr. H. Marue for the trouble of taking the X-ray photographs.

Summary.

1. In 1926 M. A. Apard reported the formation of tetranitrocentralite by the reaction of nitric peroxide upon centralite at ordinary temperature. Owing to want of his experimental data, because of the very small quantity of his sample, it seemed however so doubtful that the author was tempted to set out this investigation, and determined its chemical structure by the spectrochemical and microanalytical methods.

2. Absorption spectra have been studied on the following ten substances. 4-4′-Dinitrodiphenyldiethylurea, 2-4-2′-4′-tetranitrodiphenyldiethylurea, *p*-nitrophenylurethane, 2-4-dinitrophenylurethane, *o*-nitroacetanilide, *m*-nitroacetanilide, *p*-nitroacetanilide, *p*-nitroethylacetanilide, 2-4-6-trinitroacetanilide and 4-4′-dinitroethyldiphenylurea.

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(1) *Ber.*, **9**, 775. *Ann.*, **197**, 83.

(2) *Ber.*, **16**, 31. *Ber.*, **17**, 267.

(3) Compare *Ber.*, **41**, 3092.

3. As to the chemical constitution of the reaction product of higher melting point obtained from centralite, it has been proved to be dinitrodiphenylethylurea, which crystallizes from acetone solution in a form of very thin plates of yellowish colour, melting at 213.2–213.5°C., and hardly soluble in ordinary solvents.

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