ADDITIVE COMPOUNDS OF *m*-DINITROBENZENE

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In previous papers published in this journal attention has been drawn to the coloured additive compounds formed by the union of polynitro aromatic compounds with hydrocarbons, phenols, phenolic ethers, arylamines of different types and cyclic and unsaturated compounds.

The following is a fairly complete list of papers dealing with additive compounds of these types :—

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2. M. Berthelot, Bull. Soc. Chim., 1867, *7*, 30.
3. C. Liebermann and F. Palm, Ber., 1875, *8*, 377.
4. P. Hepp, Annalen, 1882, *215*, 356 and 375.
5. C. Marchetti, Gazetta, 1883, *12*, 502.
6. A. Smolka, Monatsh., 1885, *6*, 915.
7. O. Jacobsen, Ber., 1887, *20*, 898.
8. P. Van Romburgh, Rec. trav. chim., 1887, *6*, 366.
9. P. Van Romburgh, Rec. trav. chim., 1888, *7*, 227.
10. A. Tohl, Ber., 1888, *21*, 905.
11. J. Herz., Ber., 1890, *23*, 2540.
12. R. Von Goedike, Ber., 1893, *26*, 3042.
13. R. Behrend, Zeitsch. physikal. Chem., 1894, *15*, 183.
14. B. Kuriloff, *ibid.*, 1897, *23*, 90.
15. B. Kuriloff, *ibid.*, 1897, *23*, 676.
16. E. Bamberger and J. Muller, Ber., 1900, *33*, 102.
17. J. J. Sudborough, J. Chem. Soc., 1901, *79*, 522.
18. P. Lemoult, Compt. rend., 1902, *135*, 346.
19. E. Wedekind, Annalen, 1902, *323*, 257.
20. H. Hibbert and J. J. Sudborough, J. Chem. Soc. 1903, *83*, 1334.
21. F. Reitzenstein, J. Pr. Chem., 1903, [2], *68*, 251.

22. A. V. Saposchnikoff and P. Helwig, J. Russ. Phys. Chem. Soc., 1903, *35*, 1075.
23. A. V. Saposchnikoff and W. Rdultowsky, *ibid*, 1073.
24. A. V. Saposchnikoff and W. Rdultowsky, *ibid*, 1097.
25. G. Bruni and E. Tornani, Atti R. Accad. Lincei, 1904, [V] *13*, ii, 184.
26. C. L. Jackson and L. Clarke, Ber., 1904, *37*, 176.
27. R. Kremann, Monatsh., 1904, *25*, 1215.
28. R. Kremann, Monatsh., 1904, *25*, 1271.
29. R. Kremann, Monatsh., 1904, *25*, 1311.
30. G. Bruni and E. Tornani, Atti R. Accad. Lincei, 1905, [V], *14*, i, 154.
31. R. Kremann, Monatsh., 1905, *26*, 143,
32. R. Ciusa, Gazzetta, 1906, *36*, ii, 94.
33. R. Ciusa, and C. Agostinelli, Atti R. Accad Lincei, 1906, [V] *15*, ii, 238.
34. C. L. Jackson and L. Clarke, Proc. Chem. Soc., 1906, *22*, 83.
35. E. Noelting and E. O. Sommerhoff, Ber., 1906, 39, 76 *cf*. Sommerhoff, Dissertation, Zurich 1904.)
36. J. J. Sudborough and N. Picton, J. Chem. Soc., 1906, *89*, 592.

36 a. G. Bruni and L. Ferrari, Chem. Zeit., 1906, *30*, 568.

37. R. Ciusa and C. Agostinelli, Atti R. Accad. Lincei, 1907, [V], *16*, i, 409.
38. H. Leemann and E. Grandmougin, Ber., 1908, *41*, 1295.
39. A. Korczynski, Anzeiger Akad. Wiss. Krakau, 1908, 633, (*cf*. Chem. Zent., 1908, ii, 2010.)
40. R. Meldola, and J. G. Hay, Proc. Chem. Soc., 1908, *24*, 210.
41. G. Schultz, Ber., 1909, *42*, 2633.
42. K. A. Hofmann and H. Kirmreuther, Ber., 1910, *43*, 1764.
43. J. J. Sudborough and S. H. Beard, J. Chem. Soc., 1910, *97*, 773.
44. R. Ciusa and U. Pestalozza, Gazzetta 1911, *41*, i, 391.

45. R. Ciusa and L. Vecchiotti, Atti R. Accad. Lincei, 1911, [V], *20*, ii, 377.
46. Van Romburgh. Proc. K. Acad. Wetensch. Amsterdam, 1911, *19*, 1432 (*cf.* Chem. Zent, 1911, ii, 444).
47. J. J. Sudborough and S. H. Beard, J. Chem. Soc., 1911, *99*, 209.
48. R. Ciusa and L. Vecchiotti, Atti R. Accad. Lincei, 1912, [v], *21*, ii, 161.
49. M. Giua, Gazzetta, 1915, *45*, i, 557.
50. M. Giua, *ibid*, ii, 32.
51. M. Giua, *ibid.*, ii, 348.
52. S. T. Gadre and J. J. Sudborough, J. Chem. Soc., 1916, *109*, 1349; This Journal, 1916, *1*, 159.
53. R. Kremann and G. Grasser, Monatsh., 1916, *37*, 723.
54. R. Kremann and G. Grasser, *ibid*, 761.
55. P. Pifeiffer, Annalen, 1916, *412*, 253.
56. S. G. Sastry, J. Chem. Soc., 1916, *109*, 270; This Journal, 1916, *1*, 167.
57. J. J. Sudborough, J. Chem. Soc., 1916, *109*, 1339; This Journal, 1916, *1*, 149.
58. A. Kaufmann and V. P. de Pethard, Ber., 1917, *50*, 336.
59. A. Regenbogen, Pharm. Weekblad, 1918, *55*, 1126.
60. J. J. Sudborough, N. Picton and D. D. Karvé. This Journal, 1921, *4*, 43.
61. D. D. Karvé and J. J. Sudborough. This Journal, 1921, *4*, 159.

The additive compounds described in these papers may be classified into the following groups. The numbers given refer to the papers enumerated in the list on pp. 159—161.

1. *Additive compounds of s-trinitrobenzene.*

With aromatic hydrocarbons, 4, 54, 55

With phenols, phenolic ethers 42, 47, 57

With aromatic bases, 8, 9, 17, 20, 26, 28, 35, 42, 53,55, 57

With amino derivatives of acenapthene, fluorene, phenanthrene and anthracene, 52.

With naphthalene derivatives, 57

- With anthrols and anthramines, 52
- With ammonia, 39
- With cyclic bases, 42, 55, 56, 57
- With indene and unsaturated compounds containing the propenyl group, 30, 46
- With phenylhydrazones, and Schiff's bases, 32, 42, 45
- With hydrazine and its derivatives, 43
- With indoles, 48
- With antipyrin, 59
- With unsaturated ketones, 57
- With aromatic sulphur compounds, 57

2. *Additive compounds of s-trinitrotoluene.*

- With aromatic hydrocarbons, 4, 27, 28, 50
- With phenols and phenolic ethers, 47,
- With arylamines, 4, 17, 27, 28, 34, 50
- With Schiff's bases and phenylhydrazones, 32, 45 47
- With ammonia, 39
- With indoles and carbazole, 44, 48
- With antipyrin, 59
- With nitrated toluenes, 49
- With tetranitromethylaniline, 50

3. *Additive compounds of s-trinitroethylbenzene*, $C_2H_5\cdot C_6H_2(NO_2)_3$

- With hydrocarbons and arylamines, 41

4. *Additive compounds of* ***picric acid,*** *(s-trinitrophenol)* $OH\cdot C_6H_2(NO_2)_3$

- With hydrocarbons, 1, 2, 7, 10, 13, 15, 30, 31
- With phenols, 5, 12, 14, 15, 23, 27
- With bases, 6, 7, 18
- With aldazines, Schiff's bases and phenylhydrazones, 32, 33, 44, 45
- With unsaturated (propenyl) aromatic derivatives, 25
- With quinones, 30

5. *Additive compounds of methyl and ethyl picrate.*

- With arylamines, 17, 36

6. *Additive compounds of picryl chloride,* $C_6H_2Cl(NO_2)_3$.

With hydrocarbons, 3, 36a
With bases, 11, 16, 18, 19, 36
With diazoaminobenzene, 43
With phenylhydrazones and indoles, 37, 44, 45, 48.
With unsaturated (propenyl) compounds, 30.

7. *Additive compounds of picramide,* $NH_2 \cdot C_6H_2(NO_2)_3$.

With hydrocarbons, 3
With arylamines, 17
With diphenylmethane bases, 18

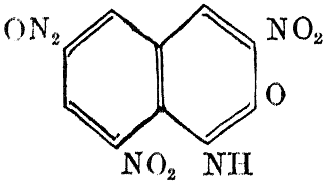
8. *Additive compounds of picrylaniline and picrylnaphthylamines.*

With *a* napthylamine, 36

9. *Additive compounds of picrylmethynitrosamine,* $NO \cdot N(CH_3) \cdot C_6H_2(NO_2)_3$.

With naphthylamines, 16.

10. *Additive compounds of trinitroquinolone,*



With hydrocarbons and phenols, 58

11. *Additive compounds of 2 : 4 - dichloro- 1 : 3 : 5 - trinitrobenzene.*

With naphthylamines 36

12. *Additive compounds of 2 : 4 : 6 - trichloro - 1 : 3 : 5-trinitrobenzene.*

With bases, 34, 36

13. *Additive compounds of trinitroacetylaminophenol.*

With *β*-naphthol, 39

14. *Additive compounds of trinitrocresol.*

With naphthalene, 24

15. *Additive compounds of tri- and tetranitro-naphthalenes.*

With hydrocarbons, phenols, phenolic ethers, arylamines and unsaturated compounds, 47, 60.

16. *Additive compounds of m-dinitrobenzene.*

With hydrocarbons, 4, 28.

With bases, 8, 9, 28, 46, 50, 53, 54, 61,

17. *Additive compounds of 2 : 4-dinitrotoluene.*

With hydrocarbons, 4, 28, 50.

With arylamines, 28, 53, 54.

18. *Additive compounds of 2 : 4-dinitrophenol.*

With naphthalene, 22.

19. *Additive compounds of 1-chloro-2 : 4-dinitrobenzene.*

With bases of diphenylmethane series, 18, 21.

20. *Additive compounds of 1 : 5-dichloro-2 : 4-dinitrobenzene.*

With naphthylamines, 36.

21. *Additive compounds of 1 : 5-dibromo-2 : 4-dinitrobenzene.*

With dimethylaniline, 34.

22. *Additive compounds of 1-chloro-2 : 4 : 6-tribromo-3 : 5-dinitrobenzene.*

With dimethylaniline, 34.

23. *Additive compounds of nitrophenols.*

With naphthylamines, 28, 53, 54.

With ammonia, 39.

24. *Additive componnds of nitrosodimethylaniline.*

With phenols and arylamines, 27, 29.

25. *Additive compounds of s-hexanitroazobenzene.*

With hydrocarbons, naphthol ethers and α-naphthylamine, 38.

From the foregoing tabular statements it is clear that the number of additive compounds prepared from *s*-trinitrobenzene and its substituted derivatives is very large, and from the examination of these compounds a certain number of generalisations have been drawn. Such generalisations include :—

(*a*) Relationships between the colour of the additive compound and the constitution of the addendum, more particularly the auxochrome effects of hydroxyl and amino or substituted amino groups (35, 43, 57).

(*b*) Relationships between the number of molecules of nitro-compound combining with one molecule of the addendum and the influence of the number of phenyl or naphthyl groups in the addendum (36a, 57).

(*c*) The influence of substituents in the trinitrobenzene molecule on its capacity for forming additive compounds (36).

(*d*) The effect of a N : C linking in the addendum on the colour of the additive compound and the deepening of the colour produced when this grouping is reduced to—NH·CH$<$ (43, 57).

(*e*) The influence of unsaturation in the addendum on its combining capacity with polynitro compounds (57) and more especially the influence of a propenyl as compared with an allyl group (25, 30, 47).

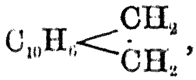
The number of compounds of *m*-dinitrobenzene and of its substitution products hitherto known has been too small to enable generalisations to be drawn and one of our objects has been to prepare a larger number of such additive compounds in order to ascertain whether in colour and composition these compounds resemble those derived from *s*-trinitrobenzene.

We have succeeded in isolating a number of additive compounds by crystallising a mixture of the two components from alcohol. Where no definite compound could be isolated under such conditions, we have, in many cases, determined the freezing point curve—temperature-concentration curve—of the two components. (Compare Philip, J.Chem. Soc., 1903, *83*, 814; Kremann, Monatsh., 1904, *25*, 1215, 1271, 1311; Ahren's Sammlung, 1909, *14*, 213).

EXPERIMENTAL.

1. *New additive compounds.*

The compounds given below were obtained by dissolving molecular quantities of the two substances in boiling alcohol and allowing the solution to cool.

1. The compound with acenaphthene  $C_{10}H_6<\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}$, $C_6H_4(NO_2)_2$, crystallises from alcohol in lemon-yellow needles, melting at 73·5°.

0·2224 gave 19·32 cc. N at 30° and 676·5 mm. N=8·71. $C_{18}H_{14}O_4N_2$ requires N=8·69 per cent.

2. The compound with β-naphthylamine, $C_{10}H_7{\cdot}NH_2$, $C_6H_4(NO_2)_2$, crystallises from alcohol in dark red needles melting at 57°.

0·1496 gave 20·41 c.c. N at 31·5° and 675·6 mm. N=13·59. $C_{16}H_{13}O_4N_3$ requires N=13·51 per cent.

3. The compound with 1-benzeneazo-2-naphthylamine, $C_6H_5N_2C_{10}H_6{\cdot}NH_2$, $C_6H_4(NO_2)_2$, crystallises from alcohol in deep red shining prisms melting at 66°.

0·1490 gave 25·11 c.c. N at 29° and 674·9 mm. N=16·92. $C_{22}H_{17}O_4N_5$ requires N=16·87 per cent.

4. The compound with aminobenzeneazodimethylaniline, $NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N(CH_3)_2$, $2C_6H_4(NO_2)_2$, crystallises from alcohol in short deep brown needles melting at 115°.

0·0992 gave 19·1 c.c. N at 25·3° and 673mm. N=19·44. $C_{26}H_{24}O_8N_8$ requires N=19·45 per cent.

5. The compound with 1:5-naphthalene-diamine, $(NH_2)_2C_{10}H_6$, $C_6H_4(NO_2)_2$, crystallises from alcohol in deep brown-black crystals melting at 78—79°.

0·1444 gave 24·3 c.c. N at 26° and 673·8 mm. N=17·04. $C_{16}H_{14}O_4N_4$ requires N=17·18 per cent.

6. The compound with 3:3′-diaminoazobenzene, $NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2$, $C_6H_4(NO_2)_2$, crystallises from alcohol in shining brown needles melting at 90—91°.

0·1294 gave 28·45 c.c. N at 24·5° and 675·2 mm. N=21·9. $C_{18}H_{16}O_4N_6$ requires N=22·1 per cent.

7. The compound with 4-aminoazonaphthalene, $C_{10}H_7\cdot N_2\cdot C_{10}H_6\cdot NH_2$, 2 $C_6H_4(NO_2)_2$, crystallises from alcohol in dark red microscopic needles melting at 122°.

0·1576 gave 24·22 c.c. N at 27° and 674·9 mm. N=15·53; $C_{32}H_{23}O_8N_7$ requires N=15·48 per cent.

8. The compound with benzyl-α-naphthylamine, $C_{10}H_7\cdot NH\cdot CH_2\cdot C_6H_5$, $C_6H_4(NO_2)_2$, crystallises from alcohol in deep orange needles melting at 63·5°.

0·1549 gave 15·95 c.c. N at 24° and 674·9 mm. N=10·51; $C_{23}H_{19}O_4N_3$ requires N=10·48 per cent.

9. The compound with 4 : 4′-diaminodiphenylamine, $NH_2\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot NH_2$, 2 $C_6H_4(NO_2)_2$, crystallises from alcohol in deep violet, nearly black, needles melting at 91—92°.

0·1050 gave 18·8 c.c. N at 26° and 676·5 mm. N=18·19; $C_{24}H_{21}O_8N_7$ requires N=18·31 per cent.

10. The compound with 3 : 3′-diaminostilbene, $NH_2\cdot C_6H_4\cdot CH : CH\cdot C_6H_4\cdot NH_2$, $C_6H_4(NO_2)_2$, crystallises from alcohol in thin feathery orange needles melting at 108—109°.

0·0890 gave 13·00 c.c. N at 23·2 and 674·7 mm. N=14·93. $C_{20}H_{18}O_4N_4$ requires N=14·82 per cent.

11. The compound with 3-animocarbazol, $\overline{C_6H_4\cdot NH\cdot C_6}H_3\cdot NH_2$, $C_6H_4(NO_2)_2$, crystallises from alcohol in violet brown prisms melting at 83—84°.

0·1016 gave 16·04 c.c. N at 25° and 676·7 mm. N=16·11; $C_{18}H_{14}O_4N_4$ requires N=16·00 per cent.

12. The compound with *o*-aminoquinoline, $(NH_2)C_9H_6N$, $C_6H_4(NO_2)_2$, crystallises from alcohol in feathery orange leaflets melting at 103—104°.

0·1164 gave 20·56 c.c. N at 24·5° and 676·0 mm. N=18·03. $C_{15}H_{12}O_4N_4$ requires N=17·94 per cent.

13. The corresponding compound with *p*-aminoquinoline crystallises from alcohol in shining red pointed prisms melting at 89—90°.

0·1213 gave 21·62 c.c. N at 27° and 674 mm. N=17·99; $C_{15}H_{12}O_4N_4$ requires N=17·94 per cent.

14. The compound with *p*-aminotetrahydroquinoline, $NH_2\cdot C_9H_{10}N$, $C_6H_4(NO_2)_2$, crystallises from alcohol in thin pale brown needles melting at 91—92°.

0·1366 gave 23·6 c.c. N at 27° and 676 mm. N=17·5 ; $C_{15}H_{16}O_4N_4$ requires N=17·72 per cent.

15. The compound with *o*-amino-*p*-toluquinoline, $CH_3 \cdot C_9H_5N \cdot NH_2, C_6H_4(NO_2)_2$, crystallises from alcohol in deep orange-red shining plates melting at 74—74·5°.

0·1160 gave 19·85 c.c. N at 25° and 677 mm. N=17·46; $C_{16}H_{14}O_4N_4$ requires N=17·18 per cent.

2. *Freezing point curves.*

The determinations of the freezing points were conducted in a small hard glass test tube, fitted with a glass stirrer and a short normal thermometer The mixture was at first completely melted and then allowed to cool, being all the while kept vigorously stirred. The temperature generally fell 2—3° below the correct freezing point and then rose. The highest point reached was taken to be the correct freezing point. Three consecutive readings never differed by more than ± 0·5°. The proportion of one of the constituents was then changed and the observations repeated. The results were then plotted on square paper as molecular percentages of *m*-dinitrobenzene against the corresponding freezing point. The curves are given in figures I and II.

The curves clearly show that there is no compound formation except in the case of 4-aminoazonaphthalene which also gives the compound when the two constituents in molecular proportions are crystallised from alcohol.

3. *Non formation of compounds.*

It has been found impossible to prepare compounds from the following substances. Those marked with an asterisk, gave only V-shaped freezing point curves, thus confirming the results of the crystallisation experiments.

Hydrocarbons :—Fluorene, anthracene, *phenanthrene, diphenyl, triphenylmethane and retene.

Primary amines :—* 2 : 4-dichloraniline, 2 : 6-dibromaniline, 2 : 4 : 6 - tribromaniline, **o*-nitraniline, * *p*-nitraniline, **m*-nitraniline, 4 - acetyl-amino - 1 -phenylazonaphthalene, *p*-aminobenzophenone, *p*-leucaniline.

Secondary amines :—*Diphenylamine, *p*-aminodiphenylamine, thiodiphenylamine, phenyl-β-naphthylamine, acetanilide.

Tertiary amines:—Dimethylaniline, dimethyl-α-naphthylamine, tetramethyldiaminothiobenzophenone, * dibenzylaniline.

Heterocyclic nitrogen compounds:— * Carbazol, *αα*-diphenylpyridine, β-imino-α-cyanohydrindene, 3-phenylpyrazolone, 1-phenyl-3-methylphrazolone, *phenylacridine, quinoline, *iso*quinoline, tetrahydro-quinoline, tetrahydroisoquinoline, *o*- and *p*-toluquinoline and the corresponding tetrahydro-compounds, α- and β-naphthaquinoline, carbostyril, 2 : 3 : 5-triphenylpyrrol.

Phenols and phenol ethers:—β-naphthol, * β-naphthol-ethyl ether.

Sulphur compound:—*Dimethylaniline disulphide.

Oximes and phenylhydrozones:—Acetophenone-oxime, Benzaldehyde-phenylthydrazone.

For the sake of comparison, the following new compounds of *β-tetranitronaphthalene* were prepared.

β-Tetranitronaphthalene-p-aminoazonaphthalene, $2 C_{10}H_4(NO_2)_4$, $NH_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_7$, crystallises from a mixture of alcohol and acetone as a deep chocolate crystalline powder melting at 240°. 0·308 gave 0·1136 hydrochloride of the base=32·8 and 0·208 β-tetranitronaphthalene=67·3. (This Journal, 1916, 1, 161). $C_{40}H_{23}O_{16}N_{11}$, requires 32·5 and 67·5 per cent respectively.

β-Tetranitronaphthalene-aminobenzeneazodimethylaniline, $2 C_{10}H_4(NO_2)_4$, $NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N(CH_3)_2$, crystallises from a mixture of alcohol and acetone in shining jet black leaflets melting at 206—207°. 0·1010 gave 20·26 c.c. N at 29° and 677 mm. N=20·2. $C_{34}H_{24}O_{16}N_{12}$ requires N=19·65 per cent.

β-Tetranitronaphthalene-tetramethyl-diaminobenzophenone $2 C_{10}H_4(NO_2)_4$, $[(CH_3)_2N{\cdot}C_6H_4]_2 : CO$, crystallises from a mixture of alcohol and acetone in shining black plates melting at 207—208°. 0·342 when treated with dilute hydrochloric acid gave 0·235 β-tetranitronaphthalene=68·7. $C_{37}H_{28}O_{17}N_{10}$, requires 69·7 per cent.

β-Tetranitronaphthalene does not form an additive compound with tetramethyldiaminodiphenylmethane.

4. *Coloured Melts*

It has been observed by many chemists, that nitro-compounds like di- and tri-nitrobenzene, di- and tri-nitrotoluene and even tetranitromethane give deeply colored mixtures with amino-compounds at high temperatures, even when no definite compound can be isolated. (Compare Korczynski, Bull. Acad. Sci. Cracow, *1908*, 333; Werner, Ber., 1909, *42*, 3424; Ostromisslensky, ibid, 1910, *43*, 197; Jsakalotos, Bull. Soc. Chim., 1912 [IV] *11*, 284; Clarke, Macbeth and Stewart, Proc. Chem. Soc., 1913, *29*, 161; Tinkler, J. Chem. Soc., 1913, *103*, 2171; Biron and Morguleva, J. Russ. Phys. Chem. Soc., 1914, *46*, 1598; Giua, Gazetta, 1915, 45, ii, 348).

The same phenomenon has been observed in the case of mixtures of *m*-dinitrobenzene with many amines. Thus the melted mixtures of dinitrobenzene and diphenylamine (deep red), aminodiphenylamine (violet) dibenzylaniline (bright orange red) *m*-nitraniline (deep orange), dimethylanilinedisulphide (bright red) completely lose their color when they solidify. Various hypotheses for explaining the formation of these colours have been brought forward, some depending upon the formation of an unstable compound, others on the change of structure of the nitro-group (*cf.* Giua and especially Tinkler (*loc. cit.*) who brings forth arguments against the supposed formation of additive compounds.)

m-Dinitrobenzene, when mixed with tetrahydro derivatives of quinoline and *iso*-quinoline, gives intensely colored solutions even at the ordinary temperature. This may be an extreme case of the same general phenomenon described above, the colour persisting even at the ordinary temperature, owing to the mixture remaining liquid.

GENERALISATIONS.

The following generalisations are based upon the observations described in previous papers by others and on the experiments described in this paper.

(1). Aromatic hydrocarbons, as a rule, do not form additive compounds with *m*-dinitrobenzene. This is based on both crystallisation experiments and also on freezing point determinations. The only exception appears to be acenaphthene.

(2). Primary arylamines combine with *m*-dinitrobenzene in equimolecular proportions (*e. g.* aniline, *α*- and *β*-naphthylamines). The stability of compounds derived from naphthalene bases is more pronounced than that of the compounds derived from the corresponding benzene derivatives (*cf.* Sudborough J. Chem. Soc., 1910, *97*, 774). Thus Romburgh (*loc. cit.*) has obtained a compound with aniline which slowly loses aniline on exposure to the atmosphere, and gives back the dinitrobenzene, while the naphthylamine compounds are thoroughly stable.

(3). The introduction of negative substituents into the arylamine inhibits the formation of additive compounds, Thus, 2 : 4-dichloraniline, 2 : 6-dibromaniline, 2 : 4 : 6-tribromaniline, *o*- , *p*- , and *m*-nitranilines, and acetanilide give no compounds.

(4). No definite rule can be laid down in the case of secondary amines. Thus benzyl-*α*-naphthylamine and diaminodiphenylamine form stable compounds, while diphenylamine, *p*-amino-diphenylamine and phenyl-*β*-naphthylamine do not combine with *m*-dinitrobenzene.

Similarly with tertiary amines; the dimethyl-*β*-naphthylamine and dimethyl-*p*-toluidine compounds have been prepared by Romburgh (*loc. cit.*) but we have failed to obtain compounds with dimethylaniline and dimethyl-*α*-naphthylamine.

(5). The presence of an additional amino- or azo- group seems to facilitate the formation of a compound. Thus diaminodiphenylamine forms a compound when both diphenylamine and *p*-aminodiphenylamine give none. Aminobenzeneazo-dimethylaniline gives a compound while dimethylaniline does not give any.

(6). Phenols and phenolic ethers do not combine with *m*-dinitrobenzene, neither do oximes or phenylhydrazones.

(7). Cyclic nitrogen compounds do not form compounds. If, however, an additional amino group is present, addition takes place. Thus carbazole, phenylacridene, substituted pyrazolones, quinoline, isoquinoline, and their tetrahydro - derivatives and carbostyril form no compounds, while definite compounds can be obtained with 3-aminocarbazole, *o*- and *p*-amino-quinolines, *o*-amino-*p*-tolu-quinoline.

(8). The combining capacity of *m*-dinitrobenzene is much less pronounced than that of *s*-trinitrobenzene or of *α* - and *β*-tetranitronaphthalenes. Many addenda which combine with these latter do not form definite compounds with *m*-dinitrobenzene. Among the compounds that have been prepared, the molecular ratio between the nitro-compound and the addendum is however the same with *m*-dinitrobenzene as with *s*-trinitrobenzene. The colours of the dinitro-compounds are a shade lighter and the melting points considerably lower than those of the corresponding trinitro-compounds (see Table I.)

(9). The introduction of CH_3, Cl, Br, OH into the molecule of *m*-dinitrobenzene does not affect the relative proportions of the combining compounds provided addition occurs, *e. g.* the compounds with naphthalene, aniline, *α*- and *β*-naphthylamines.

Exceptions however, are met with in the additive compounds formed from tetramethyl-diaminodiphenylmethane and tetramethyldiamino-benzophenone and *m*-dinitrobenzene and chloro-*m*-dinitrobenzene. (*cf.* Nos. 18 and 46.)

(10). Similarly the introduction of CH_3, OH, OCH_3, C_2H_5, $CO_2C_2H_5$, Cl, Br, NH_2, NHC_6H_5 into the trinitrobenzene molecule does not affect the molecular composition of the additive compound provided addition takes place, *e.g.* the compounds with benzene, naphthalene, anthracene, aniline, *α*-naphthylamine, *β*-naphthylamine, dimethylaniline, ethyl-*α*-naphthylamine, dimethyl-*α*-naphthylamine, *p*-toluidine, benzidine, the phenylhydrazones, substituted indoles and unsaturated compounds.

An exception is met with, however, in the case of *s*-trichloro-trinitrobenzene which unites with *α*-naphthylamine in the molecular proportions 2 : 1 (*cf.* 36) whereas *s*-trinitrobenzene and *α*-naphthylamine unite in equimolecular proportions.

(11). On the whole there is greater similarity between the additive compounds of *m*-dinitrobenzene, *s*-trinitrobenzene and *β*-tetranitronaphthalene as regards the molecular proportions in which they combine with the various addenda than in the case of *α*-trinitronaphthalene.

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TABLE I.

Addendum.	m - Dinitrobenzene.				s - Trinitrobenzene.				α - Trinitronaphthalene.				β - Tetranitronaphthalene.			
	Mols. of nitro-compound : mols. of addendum	Appearance.	M. P.	*Authority.	Mols. of nitro-compound : mols. of addendum.	Appearance.	M. P.	*Authority.	Mols. of nitro-compound : mols. of addendum.	Appearance.	M. P.	*Authority.	Mols. of nitro-compound : mols. of addendum.	Appearance.	M. P.	*Authority.
Hydrocarbons.																
1. Naphthalene	1 : 1	Thin prismatic needles (very unstable)	52—53°	4	1 : 1	Pale yellow needles	152·5°	57					1 : 1	Slender lemon-yellow needles	191-192°	60
2. Anthracene					1 : 1	Scarlet needles	164°	57					1 : 1	Deep red shining needles	212-214°	60
3. Phenanthrene					1 : 1	Glistening orange needles or plates	158°	57					1 : 1	Orange yellow needles	243°	60
4. Acenaphthene	1 : 1	Lemon-yellow needles	73·5°	61	1 : 1	Golden yellow needles	168°	57					1 : 1	Shining deep red prisms	125°	60
Primary Amines.																
5. Aniline	1 : 1	Red solid	42°	43	1 : 1	Red leaflets	123—124°	5					1 - 1	Dark brown solid	154°	60
6. α - Naphthylamine	1 : 1	Red needles	67°	46	1 : 1	Brick-red prisms	123°	18	2 : 1	Purple-black prisms	135·5°	60	1 : 1	Deep brown needles	204-205°	60
7. α - Acetnaphthalide					1 : 1	Sulphur-yellow needles	140·5°	18					1 : 1	Slender yellow needles	184-185°	60
8. β - Naphthylamine	1 : 1	Red needles	57°	61	1 : 1	Deep brick-red needles	162°	18	2 : 1	Dark purple red needles	145·5—146°	60	1 : 1	Deep brown plates	211-212°	
9. β - Acetnaphthalide					1 : 1	Sulphur-yellow needles	142°	18					1 : 1	Golden yellow needles	200-201°	60
10. Benzidine	1 : 1	Black needles	128°	46	1 : 1	Black needles	—	36	2 : 1	Black prisms	138°	60	1 : 1	Black prisms	194°	60
11. Anisidine					1 : 1	Brownish red plates	95°	43	1 : 2	Black crystals	128°	60				
12. Psuedo - cumidine					1 : 1	Red solid	—	36	1 : 1	Black prisms	101°	60	1 : 1	Black needles	155°	60

TABLE I.—*Continued.*

Addendum.	*m* - Dinitrobenzene .				*s* - Trinitrobenzene				*a* -Trinitronaphthalene.				*β*-Tetranitronaphthalene.			
	Mols. of nitro-compound : mols. of addendum.	Appearance.	M. P.	*Authority.	Mols. of nitro-compound : mols. of addendum.	Appearanee.	M. P.	*Authority.	Mols. of nitro-compound : mols. of addendum.	Appearance.	M. P.	*Authority.	Mols. of nitro-compound : mols. of addendum.	Appearance.	M. P.	*Authority.
13. 1 : 5-Naphthylenediamine	1 : 1	Deep brown-black crystals	78—79°	61	1 : 1	Deep brown needles	245°	43	1 : 1	Thin black needles	243° (decomp	60				
14. *p* - Aminobenzeneazo-dimethylaniline.	2 : 1	Short deep brown needles	5°	61	2 : 1	Deep brown plates	157-158°	43					2 : 1	Shining black leaflets	207°	61
15. 1 - Benzeneazo-*β* - naphthylamine.	1 : 1	Deep red shining prisms	66°	61	1 : 1	Dark red featherly needles	153°	43								
16. 3 : 3' -Diaminostilbene	1 : 1	Featherly orange needles	108-109°	61	1 ; 1	Deep purple-brown needles	190—191 °	43								
Secondary Amines.																
17. 3 : 3 -Diaminoazobenzene	1 : 1	Shining brown needles	90—91°	61	1 : 1	Dark red-brown needles	188°	43								
18. 4 - Aminoazonaphthalene	2 : 1	Small dark red needles	122°	61	2 : 1	Brilliant black needles	232—233°	57					2 : 1	Deep chocolate crystalline powder	238-240°	61
19. Ethyl - *a* - naphthylamine					1 : 1	Brick-red needles	153·5-154°	21	1 : 1	Reddish black needles	109°	60	1 : 1	Black needles	134°	60
20. Phenyl -*β* - naphthylamine.					2 : 1	Deep reddish brown plates	115·5°	43					1 : 1	Deep violet-brown needles	174-175°	60
					1 : 1	Brick red needles	109°						1 : 1	Minute, deep black needles	164-165°	60
21. Benzyl - *a* - naphthylamine.	1 : 1	Deep orange needles	63.5°	61	1 : 1	Chocolate-red needles	174-174·5°	43								
22. *p* - Tolyl - *β*-naphthylamine					2 : 1	Crismson-red plates	120·5-121°	43					1 : 1	Shining black needles	150°	60
23. Diphenylamine	3 : 4	Intense red liquid	—	61	2 : 1	Shining black plates	109—110°	38	2 : 1	Dark red needles	101°	60	2 : 1	Black needles	185°	60

FIGURE I.

Freezing point Curves *m*-Dinitrobenzene with various Aromatic Compounds.

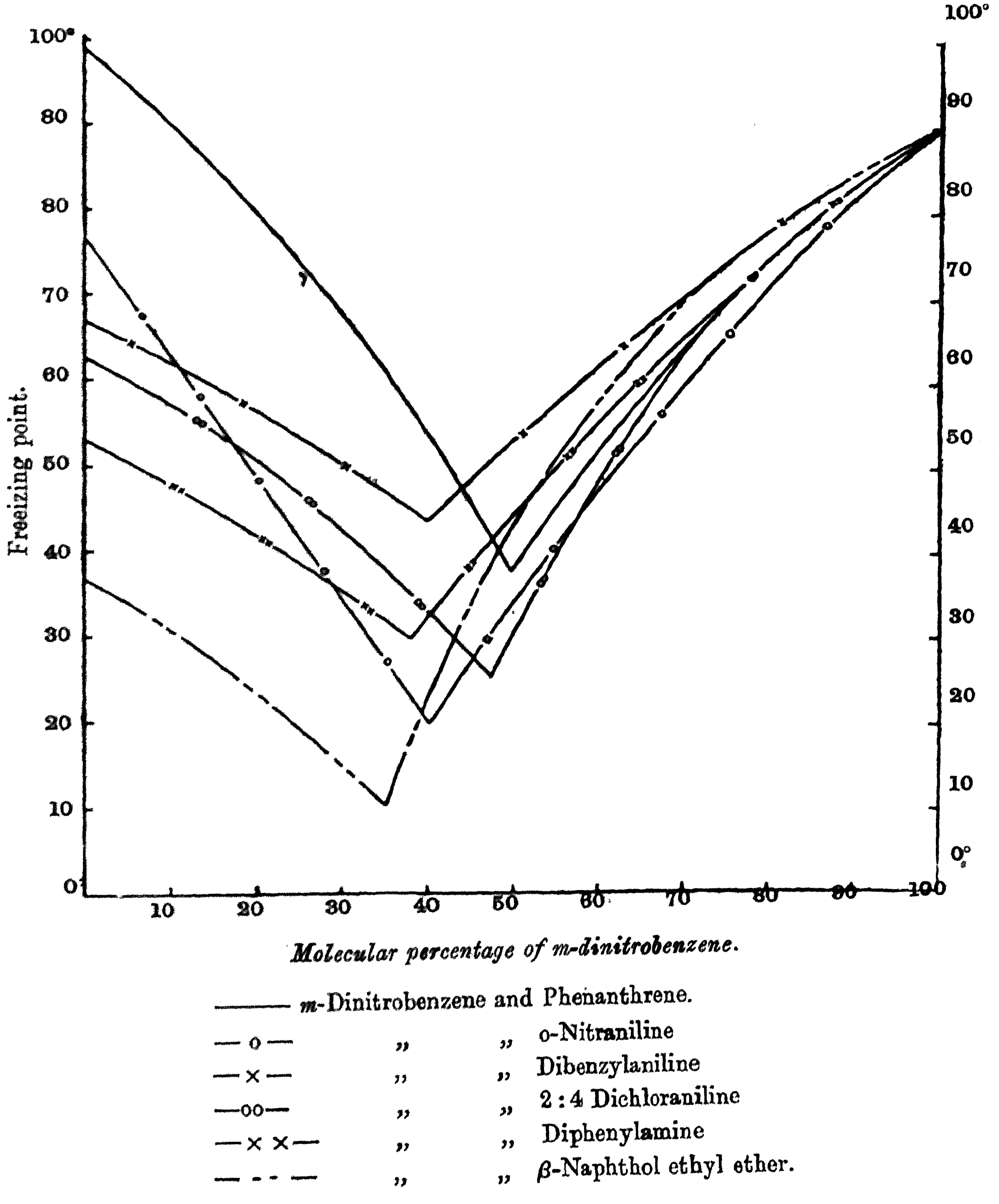

FIGURE II.

Freezing-point Curves of *m*-Dinitrobenzene with various Aromatic Compounds.