172. *The Existence of Aromatic Bisnitroso-compounds of the Type* R'N$_2$O$_2$R''.

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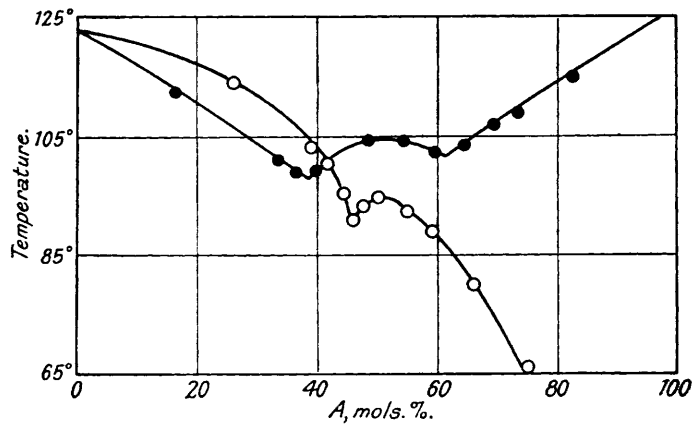
There is no *a priori* reason why mixed bimolecular aromatic nitroso-compounds of the type R'N$_2$O$_2$R'' should not exist with a stability at least of the same order as that of the ordinary bimolecular forms. The present investigation was therefore undertaken in the expectation that such mixed forms would readily be obtained, and in the hope that, by varying the polar nature of the substituents in the aryl groups R' and R'', unsymmetrical bisnitroso-compounds might be obtained of sufficient stability for their individual chemical properties to be studied in the absence of their dissociation products. We have, however, found only two examples of solid mixed bisnitroso-compounds capable of existence in solid–liquid equilibrium; but evidence has been obtained from cryoscopic measurements in benzene of the presence of mixed bimolecular nitroso-molecules in some cases where the solid compounds apparently do not exist.

Experimental.

Solid–liquid equilibria were investigated in a number of two-component mixtures of aromatic nitroso-compounds. The usual methods for determining equil. temps. were unsuitable. The



● = o-*Nitronitrosobenzene* (A)–*nitrosomesitylene*.
○ = 4-*Nitroso*-m-*xylene* (A)–*nitrosomesitylene*.

construction of heating and cooling curves, or the observation of the temps. at which small particles of solid phase are just in equilibrium with liquids of known composition, involves the maintenance of the nitroso-compounds for considerable periods of time at temps. at which decomp. takes place. A modification of the latter method was therefore adopted, whereby very small quantities of solid could be heated comparatively rapidly to the temp. of solid–liquid equilibrium. Mixtures of known composition of the two components were fused to ensure complete mixing and rapidly chilled. The solid mixture was then powdered and introduced into capillary tubes; these were fixed to a thermometer and heated in an oil-bath. The solid was observed with a lens, the "eutectic softening" being usually easily detected ($\pm$ 1·0°) owing to the distinctive green colour of the first trace of liquid nitroso-compound formed. The temp. of disappearance of the last crystal of solid phase was reproducible, with different specimens of the same mixture, to within at most $\pm$ 0·5°, and in all cases a mean of at least three determinations was taken.

The nitroso-compounds examined were prepared by standard methods. The data obtained are given in Table I. The temps. T_1 and T_2 are those of solid–liquid equilibrium and of incipient fusion (eutectic softening) respectively. Points on the solidus curve (T_2) are given only where there is clear evidence of solid solution.

The data for the systems of nitrosomesitylene with 4-nitroso-*m*-xylene and with *o*-nitronitrosobenzene are plotted in the fig., where the curves show in each case the existence of an

TABLE I.

p-Nitrosotoluene (A) and nitrosobenzene.

A, mols. %.	T_1.	T_2.
0·0	68·0°	—
27·8	53·9	31·0°
33·6	50·4	32·0
41·1	46·0	31·0
44·7	45·5	32·0
53·3	40·5	31·0
58·1	38·2	28·0
63·2	33·5	29·0
67·0	32·0	31·5
78·0	36·0	33·5
89·5	42·0	39·5
100·0	47·0	—

o-Nitrosoanisole (A) and *p*-bromonitrosobenzene.

A, mols. %.	T_1.	T_2.
0·0	92·8°	—
5·8	90·2	70·0°
14·0	87·8	69·5
25·4	84·5	69·0
33·1	80·3	70·0
40·7	78·2	70·0
49·9	73·9	72·0
59·0	78·2	70·0
68·1	84·6	71·0
77·4	90·0	70·0
91·2	96·4	72·0
100·0	101·7	—

m-Nitronitrosobenzene (A) and *p*-nitrosodimethylaniline.

A, mols. %.	T_1.	T_2.
0·0	85·0°	—
6·0	80·0	71·0°
16·8	71·0	59·0
24·0	64·1	54·5
33·5	55·8	51·5
46·2	55·5	51·0
57·2	66·5	51·5
64·5	73·0	60·0
72·7	80·0	69·5
88·6	87·1	80·5
93·4	88·5	81·0
100·0	90·0	—

o-Nitrosotoluene and nitrosobenzene (A).

A, mols. %.	T_1.	T_2.
0·0	72·0	—
7·9	63·0	57·0
21·5	57·9	50·0
27·4	55·2	45·0
33·1	53·0	46·0
41·1	50·2	42·0
47·0	48·8	44·0
51·0	48·9	44·0
53·2	49·8	45·0
55·7	51·9	44·0
69·2	60·4	44·0
84·8	67·0	46·0
100·0	68·0	—

o-Nitrosotoluene (A) and *p*-nitrosotoluene.

A, mols. %.	T_1.	T_2.
0·0	47·0	—
7·6	41·6	34·0
18·5	37·7	32·0
23·6	35·7	33·0
26·9	34·2	33·0
29·8	35·0	33·0
39·6	42·0	30·5
45·1	46·5	33·0
52·3	50·9	—
69·7	61·5	—
79·5	65·4	35·0
89·0	67·6	45·0
100·0	72·0	—

p-Bromonitrosobenzene (A) and *m*-nitronitrosobenzene.

A, mols. %.	T_1.	T_2.
0·0	90·0	—
5·5	88·5	80·0
7·8	87·5	78·0
14·2	85·0	70·0
21·5	82·5	67·0
30·6	79·5	67·0
44·9	71·0	67·0
51·7	76·1	67·0
60·5	82·0	67·0
73·3	86·9	70·0
79·4	88·0	75·5
89·8	91·0	82·0
100·0	93·0	—

o-Nitronitrosobenzene (A) and nitrosomesitylene.

A, mols. %.	T_1.	T_2.
0·0	122·0	—
16·5	112·3	90·0
22·7	108·5	92·0
33·7	101·0	—
34·8	100·2	90·0
36·5	99·0	—
39·8	99·0	91·0
48·2	104·0	99·0
54·2	104·2	99·0
59·9	102·1	101·0
64·5	103·5	99·0
69·7	107·0	—
73·6	109·1	101·0
82·5	115·0	101·0
100·0	126·0	—

Nitrosomesitylene (A) and *o*-nitrosotoluene.

A, mols. %.	T_1.	T_2.
0·0	72·0	—
13·0	66·2	53·0
23·8	61·2	55·0
29·5	58·7	54·0
32·5	57·0	53·0
34·8	55·2	54·0
39·7	80·4	56·0
43·5	85·0	54·0
47·6	89·5	56·0
50·8	93·0	56·0
54·9	96·0	55·0
64·2	101·9	54·0
70·5	106·1	56·0
100·0	122·0	—

4-Nitroso-*m*-xylene (A) and nitrosomesitylene.

A, mols. %.	T_1.
0·0	122·0
26·0	114·0
39·0	103·0
41·8	100·5
44·0	95·1
46·0	91·0
47·2	93·0
50·0	94·5
54·9	92·0
59·1	89·0
66·0	80·0
75·1	66·3
89·2	36·2
96·0	35·1
100·0	42·5

o-Nitrosoanisole (A) and nitrosomesitylene.

A, mols. %.	T_1.	T_2.
0·0	122·0	—
30·1	108·0	69·0
37·0	102·6	—
48·0	92·2	70·0
56·5	83·0	70·0
65·7	78·6	69·0
88·0	93·0	73·0
100·0	101·7	—

s-Tribromonitrosobenzene (A) and nitrosomesitylene.

A, mols. %.	T_1.
0·0	122·0°
10·0	117·5
27·8	108·0
39·8	98·2
46·0	97·1
53·3	100·6
62·9	105·0
79·0	112·2
100·0	120·0

4-Nitroso-*m*-xylene (A) and *o*-nitrosotoluene.

A, mols. %.	T_1.
0·0	72·0°
19·0	65·1
29·9	60·5
39·2	56·5
48·0	51·0
51·2	47·3
59·3	38·5
69·1	27·0
78·0	35·5
100·0	42·5

m-Nitronitrosobenzene (A) and nitrosomesitylene

A, mols. %.	T_1.
0·0	122·0°
20·0	110·0
26·2	106·1
34·8	98·2
50·0	86·0
59·0	74·5
66·2	66·2
78·8	75·0
91·3	85·0
100·0	90·0

equimol. bisnitroso-compound with congruent m. p. The plots for the remainder of the systems show no indication of compound formation. In several cases evidence has been obtained of partial miscibility in the solid phases.

Evidence for the existence of certain mixed bisnitroso-molecules in solution has been obtained from measurements of the depressions of the f. p. of C_6H_6 by two nitroso-compounds separately and in the presence of each other. If no interaction occurred, the depression produced by the mixture would be the sum of those caused by each nitroso-compound separately; but if interaction took place, the resulting diminution in the total number of solute molecules would lead to a calc. mol. wt. greater than the mean mol. wt. of the mixed solute. The data for the four pairs of nitroso-compounds given in Table II were obtained by first finding the f. p. of a solution containing a fixed quantity of the first component and then determining the f. p.'s after successive additions of small quantities of the second component. The depressions thus caused, when plotted against the wts. of the second component, give satisfactory straight lines passing through the origin, from the slope of which mean apparent mol. wts. were calculated.

The cryoscopic constants K of the two different specimens of C_6H_6 used were found from preliminary expts. with pure $C_{10}H_8$. The f. p. depressions given in Table II refer to 20 g. of C_6H_6 containing the wts. of solute recorded. ΔT_0 is the depression produced by the addition of the first component (A); the values of ΔT are the subsequent depressions caused by successive additions of the second solute (B). M^0_B is the formula weight of unimolecular B.

TABLE II.

o-Nitrosotoluene (A); *p*-bromonitrosobenzene (B).
$K = 51{\cdot}2$; A = 0·1487 g.; $\Delta T_0 = 0{\cdot}304°$.

B, g.	ΔT.	B, g.	ΔT.
0·0261	0·042°	0·1942	0·272°
0·0703	0·109	0·3044	0·414
0·1410	0·202		

(Mean) $M_B = 186$; $M^0_B = 186$.

p-Bromonitrosobenzene (A); *o*-nitrosotoluene (B).
$K = 51{\cdot}2$; A = 0·2362 g.; $\Delta T_0 = 0{\cdot}322°$.

B, g.	ΔT.	B, g.	ΔT.
0·0741	0·149°	0·1500	0·290°
0·1140	0·222	0·1678	0·338

(Mean) $M_B = 126$; $M^0_B = 121$.

o-Nitrosotoluene (A); nitrosomesitylene (B).
$K = 51{\cdot}2$; A = 0·1518 g.; $\Delta T_0 = 0{\cdot}312°$.

0·0192	0·024	0·1116	0·121
0·0441	0·044	0·1848	0·186

(Mean) $M_B = 251$; $M^0_B = 149$.

Nitrosomesitylene (A); *o*-nitrosotoluene (B).
$K = 51{\cdot}2$; A = 0·3286 g.; $\Delta T_0 = 0{\cdot}158°$.

0·0710	0·123	0·1807	0·319
0·1196	0·209	0·2170	0·375
0·1541	0·270		

(Mean) $M_B = 148$; $M^0_B = 121$.

o-Nitrosoanisole (A); nitrosomesitylene (B).
$K = 52{\cdot}2$; A = 0·0994 g.; $\Delta T_0 = 0{\cdot}250°$.

0·0217	0·024	0·1030	0·094
0·0425	0·039	0·1552	0·142
0·0729	0·068		

(Mean) $M_B = 280$; $M^0_B = 149$.

Nitrosomesitylene (A); *o*-nitrosoanisole (B).
$K = 52{\cdot}2$; A = 0·1862 g.; $\Delta T_0 = 0{\cdot}152°$.

0·0530	0·078	0·1307	0·199
0·0895	0·136	0·1667	0·263

(Mean) $M_B = 161$; $M^0_B = 137$.

ω-Nitrosotoluene (A); nitrosomesitylene (B).
$K = 51{\cdot}2$; A = 0·1026 g.; $\Delta T_0 = 0{\cdot}292°$.

0·0235	0·024	0·1023	0·106
0·0548	0·056	0·1195	0·120
0·0822	0·081		

(Mean) $M_B = 256$; $M^0_B = 149$.

Nitrosomesitylene (A); ω-nitrosotoluene (B).
$K = 51{\cdot}2$; A = 0·1783 g.; $\Delta T_0 = 0{\cdot}155°$.

0·0280	0·030	0·1251	0·135
0·1087	0·116	0·1537	0·163

(Mean) $M_B = 237$; $M^0_B = 121$.

The apparent mol. wts. in C_6H_6 of the components of the above mixtures of nitroso-compounds, with the exception of ω-nitrosotoluene, have already been reported (Hammick, J., **1931**, **3105**). The mol. wt. of the latter substance [M = **242** for $(CH_2Ph{\cdot}NO)_2$] in HOAc has been determined by Behrend and König (*Annalen*, 1891, **263**, 212); they found values of **257** and **263**, which point to association of the nitroso-compound above bimolecular and are probably not accurate. In benzene ($K = 51{\cdot}2$) we find the following depressions of f. p. for 20 g. of C_6H_6.

Wt. solute, g.	0·0321	0·0686	0·1026	0·1492
ΔT	0·037°	0·081°	0·120°	0·175°

From the slope of the ΔT–concn. line, we find $M_{obs.}$ = **220**, which indicates that the association is $x = 100\ (M_{obs.} - M^0)/M^0 = 82\%$ (where M^0 refers to the simple molecule).

In Table III are given (1) the apparent mol. wts. in C_6H_6 of each of the components of the mixed solutes taken separately, (2) the apparent mol. wts. of each solute in the presence of the other, (3) the formula weight of the simple molecule, M^0_B. Examination of the results shows no appreciable compound formation for the first pair. For the second and third pairs the data show definite indications of intermolecular compound formation, which is not revealed

TABLE III.

1st Solute (A).	2nd Solute (B).	M_B.	M_B (in presence of A).	M_B^0.
o-Nitrosotoluene	*p*-Bromonitrosobenzene	189	186	186
p-Bromonitrosobenzene	*o*-Nitrosotoluene	131	126	121
Nitrosomesitylene	*o*-Nitrosotoluene	131	148	121
o-Nitrosotoluene	Nitrosomesitylene	234	251	149
Nitrosomesitylene	*o*-Nitrosoanisole	145	161	137
o-Nitrosoanisole	Nitrosomesitylene	234	280	149
ω-Nitrosotoluene	Nitrosomesitylene	234	256	149
Nitrosomesitylene	ω-Nitrosotoluene	224	237	121

by the solid–liquid equilibria data. The results for the ω-nitrosotoluene–nitrosomesitylene system, where interaction is again found, are of special interest in that they appear to show that true ω-nitrosotoluene molecules, $CH_2Ph{\cdot}NO$, exist as such in C_6H_6 solution, and that transformation into the isomeric aldoxime is at any rate not complete. It was not possible to investigate solid–liquid equilibria in this system owing to the instability of ω-nitrosotoluene above its m. p.

SUMMARY.

Solid–liquid equilibria have been investigated in a number of two-component mixtures of aromatic nitroso-compounds. Congruent-melting mixed bisnitroso-compounds of the type $R'N_2O_2R''$ have been found in the systems 4-nitroso-*m*-xylene–nitrosomesitylene and *o*-nitronitrosobenzene–nitrosomesitylene.

Cryoscopic measurements in benzene solution show the presence of unsymmetrical bisnitroso-molecules in mixtures of nitrosomesitylene with *o*-nitrosotoluene, *o*-nitrosoanisole, or ω-nitrosotoluene.

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