30. *The Associating Effect of the Hydrogen Atom. Part V. Nitroarylhydrazones.*

By Louis Hunter and John A. Marriott.

Cryoscopic measurement has been made of the molecular weights of a number of nitro-substituted arylhydrazones over a range of concentration. The results provide direct evidence of a type of hydrogen-bond association long assumed on theoretical grounds to be operative in certain substances, *viz.*, that due to the union of unlike groups in separate molecules.

Two different kinds of hydrogen-bond association are therefore distinguishable:

1. *Homogeneous association*—between typical associating groups of the same kind, as in phenols (—OH-----HO—), oximes (=NOH-----HON=), amides (—CO·NHR-----NHR·CO—), etc.
2. *Heterogeneous association*—between electron-donor and electron-acceptor groups of different kinds, *e.g.*, —NO_2-----HO—, —NO_2-----HNAr·N=, and presumably many others.

There are many examples of the enhancement of the molecular association of phenols as a result of the further substitution of an electron-donor group. This increased association is presumably due to the greater variety of intermolecular hydrogen bonds made possible by the union of hydroxyl with the new group. The latter mode of association, which we propose to call the " heterogeneous " mechanism (see Summary), partly supersedes and partly coexists with the " homogeneous " mechanism, due to union between hydroxyl groups alone; the result is usually to increase the proportion of associated molecules. Chelation in *o*-nitrophenol and numerous similar examples is obviously an intramolecular manifestation of the heterogeneous effect, but naturally leads, in this special sense, to a unimolecular state. An attempt at the quantitative assessment of the above two types of association has been made in the case of many substituted phenols by Lassettre (*Chem. Reviews*, 1937, **20**, 291), who, by a comparison of the factors of association of substituted and unsubstituted phenols, arrives at some measure of the relative bond strength in both types of association.

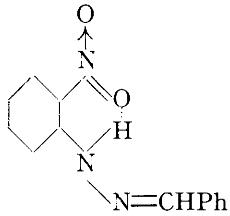
No *direct* evidence of the heterogeneous effect is possible unless a group can be found which, whilst being a potentially proton-donor group, shows little or no tendency to homogeneous association. A search of the literature reveals that such a condition might be fulfilled in the arylhydrazone group (=N·NHAr), for the work of von Auwers and his students (*Z. physikal. Chem.*, 1896, **21**, 337; *Ber.*, 1900, **33**, 1302) contains examples of the feeble association of aldehyde and ketone phenylhydrazones : but introduction of a nuclear nitro-group greatly increases the degree of association. That the association of the phenylhydrazones, though feeble, is appreciable, is shown by further examples in the present work (Fig. 1), and especially by a comparison of their degree of association with that of substances in which the imino-hydrogen atom has been either replaced by other groups, as in $CHAr{:}N{\cdot}NRPh$, or is engaged in chelate ring formation, as in benzaldehyde-*o*-nitrophenylhydrazone (II). In these substances the association is completely checked. Independent evidence exists (Hunter and Marriott, J., 1937, 2000) of the electron-donor properties of the tertiary nitrogen atom in the phenylhydrazones, and it seems clear that the weak homogeneous association of these substances is due to union between the donor atom (═N—) in one molecule with the imino-hydrogen atom in another.

By an examination of the molecular condition of a further number of nitroarylhydrazones, the suitability of the phenylhydrazone grouping as a means of detecting heterogeneous association has been fully confirmed. The conclusion has been reached that a high degree of molecular association occurs in the nitroarylhydrazones whenever the nitro- and the hydrazone-groups in separate molecules are free to unite by means of a hydrogen bond, *viz.*, $—NO_2{\cdots}H—NAr{\cdot}N═$. The following is a summary of the results leading to this conclusion.

1 (See Fig. 1). Benzaldehydephenylhydrazone (I) is weakly associated. Substitution of a nitro-group in either phenyl nucleus, as in *o*-, *m*-, and *p*-nitrobenzaldehydephenylhydrazones and benzaldehyde-*p*-nitrophenylhydrazone, causes a high degree of association. Benzaldehyde-*o*-nitrophenylhydrazone (II), in which the hydrogen bonding can occur intramolecularly, is found to be unassociated.

$Ph{\cdot}CH═N{\cdot}NHPh$

(I.)



(II.)

(*p*-) $NO_2{\cdot}C_6H_4{\cdot}CH═N{\cdot}NRPh$

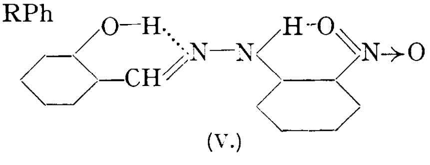
(III.)

2 (See Fig. 2). Substitution of a methyl or phenyl group for the imino-hydrogen atom of the nitrobenzaldehydephenylhydrazones checks association; *e.g.*, *o*-, *m*- and *p*-nitrobenzaldehyde-phenylmethylhydrazones (III; R = Me) and -diphenylhydrazones (III; R = Ph) are all unassociated.

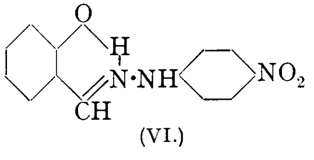
3 (See Fig. 3). In the unlikely event of the hydrogen of the methin group being concerned in hydrogen-bond formation, the effect of its replacement by methyl was examined : *m*-nitroacetophenonephenylhydrazone (IV; R = H) was found to be associated, but the corresponding *diphenylhydrazone* (IV; R = Ph) is unassociated. By dispensing with the nitro-group (as in acetophenonephenylhydrazone) and the imino-hydrogen atom (as in acetophenonediphenylhydrazone) association is again checked.

(*m*-) $NO_2{\cdot}C_6H_4{\cdot}CMe═N{\cdot}NRPh$

(IV.)

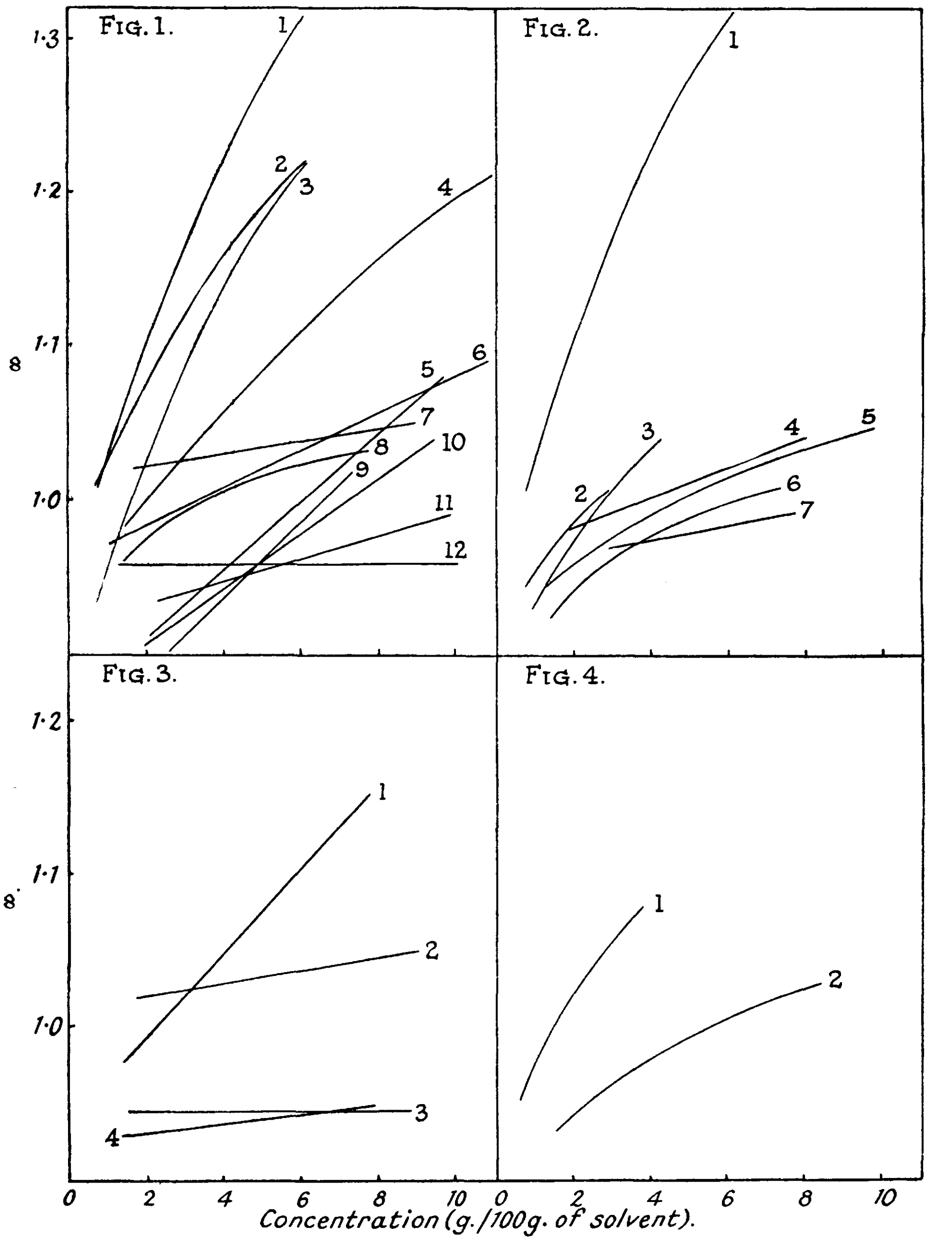


(V.)



(VI.)

4 (See Fig. 4). The case of the isomeric salicylidenenitrophenylhydrazones is of interest. The *o*-compound is unassociated in naphthalene solution, and it is evident that both hydroxyl- and imino-hydrogen atoms are chelated (V), and therefore not free to undertake intermolecular bonding. On the other hand, salicylidene-*p*-nitrophenylhydrazone (VI) is associated, and since there is independent evidence (Hunter and Marriott, *loc. cit.*) of chelation of the hydroxyl hydrogen, it seems clear that association is due to intermolecular union of the nitro- and the hydrazone-groups. The melting-point depressions of these



KEY TO FIGS. 1–4.

Fig. 1.—1 = p-*Nitrobenzaldehydephenylhydrazone* (III; R = H). 2 = m-*Nitrobenzaldehydephenylhydrazone*. 3 = o-*Nitrobenzaldehydephenylhydrazone*. 4 = *Benzaldehyde*-p-*nitrophenylhydrazone*. 5 = p-*Tolualdehydephenylhydrazone*. 6 = *Acetonephenylhydrazone*. 7 = *Acetophenonephenylhydrazone*. 8 = *Benzaldehyde*-o-*nitrophenylhydrazone* (II). 9 = *Benzaldehydephenylhydrazone* (I). 10 = *Benzaldehyde*-p-*tolylhydrazone*. 11 = p-*Methylacetophenonephenylhydrazone*. 12 = *Benzophenonephenylhydrazone*.

Fig. 2.—1 = p-*Nitrobenzaldehydephenylhydrazone* (*for comparison*). 2 = p-*Nitrobenzaldehydephenylmethylhydrazone* (III; R = Me). 3 = m-*Nitrobenzaldehydephenylmethylhydrazone*. 4 = o-*Nitrobenzaldehydephenylmethylhydrazone*. 5 = p-*Nitrobenzaldehydediphenylhydrazone* (III; R = Ph). 6 = m-*Nitrobenzaldehydediphenylhydrazone*. 7 = o-*Nitrobenzaldehydediphenylhydrazone*.

Fig. 3.—1 = m-*Nitroacetophenonephenylhydrazone* (IV; R = H). 2 = *Acetophenonephenylhydrazone*. 3 = *Acetophenonediphenylhydrazone*. 4 = m-*Nitroacetophenonediphenylhydrazone* (IV; R = Ph).

Fig. 4.—1 = *Salicylidene*-p-*nitrophenylhydrazone* (VI). 2 = *Salicylidene*-o-*nitrophenylhydrazone* (V).

FIG. 1.

	Concn.	*M.*	*a.*
p-Nitrobenzaldehydephenylhydrazone ($C_6H_4Br_2$)	*0·67*	*244*	*1·01*
	2·80	*285*	*1·18*
	3·50	*280*	*1·16*
	6·02	*315*	*1·31*
m-Nitrobenzaldehydephenylhydrazone ($C_6H_4Br_2$)	*0·64*	*244*	*1·01*
	1·46	*256*	*1·06*
	1·81	*261*	*1·08*
	3·31	*274*	*1·14*
	4·68	*290*	*1·20*
	6·18	*294*	*1·22*
o-Nitrobenzaldehydephenylhydrazone ($C_6H_4Br_2$)	*0·62*	*225*	*0·93*
	1·64	*243*	*1·01*
	3·25	*275*	*1·14*
	6·11	*295*	*1·22*
Benzaldehyde-*p*-nitrophenylhydrazone ($C_{10}H_8$)	1·325	236	0·98
	2·83	250	1·035
	4·73	262	1·09
	8·39	281	1·16
	11·90	293	1·22
p-Tolualdehydephenylhydrazone ($C_6H_4Br_2$)	1·57	183	0·87
	3·47	198	0·94
	5·66	208	0·99
	8·09	218	1·04
	9·72	226	1·08
Acetonephenylhydrazone (C_6H_6)	0·96	143	0·97
	3·24	146	0·99
	4·06	149	1·01
	5·70	150	1·02
	8·33	154	1·05
	10·76	160	1·09

	Concn.	*M.*	*a.*
Acetophenonephenylhydrazone (C_6H_6)	1·81	213	1·02
	3·51	212	1·01
	5·70	215	1·02
	7·10	217	1·03
	8·94	221	1·05
Benzaldehyde-*o*-nitrophenylhydrazone ($C_{10}H_8$)	1·41	231	0·96
	3·16	240	1·00
	5·23	243	1·01
	6·61	246	1·02
	7·71	249	1·03
Benzaldehydephenylhydrazone ($C_6H_4Br_2$)	2·15	175	0·89
	3·83	180	0·92
	5·32	190	0·97
	7·20	200	1·02
Benzaldehyde-*p*-tolylhydrazone ($C_6H_4Br_2$)	2·05	191	0·91
	4·56	199	0·95
	5·71	209	0·99
	7·64	212	1·01
	9·43	218	1·04
p-Methylacetophenonephenylhydrazone ($C_6H_4Br_2$)	2·28	208	0·93
	4·77	215	0·96
	6·97	217	0·97
	8·24	220	0·98
	9·86	222	0·99
Benzophenonephenylhydrazone ($C_{10}H_8$) (From von Auwers and Orton, *Z. physikal. Chem.*, 1896, **21**, 337).	*1·28*	*260*	*0·96*
	3·42	*261*	*0·96*
	6·39	*259*	*0·96*
	9·98	*262*	*0·96*

FIG. 2 [includes *p*-nitrobenzaldehydephenylhydrazone (Fig. 1) for comparison].

	Concn.	*M.*	*a.*
o-Nitrobenzaldehydephenylmethylhydrazone (C_6H_6)	1·91	251	0·98
	3·96	256	1·00
	5·92	260	1·02
	8·05	265	1·04
m-Nitrobenzaldehydephenylmethylhydrazone (C_6H_6)	0·80	237	0·93
	1·86	249	0·975
	3·17	259	1·015
	4·23	266	1·04
p-Nitrobenzaldehydephenylmethylhydrazone (C_6H_6)	0·72	239	0·94
	1·13	249	0·975
	1·86	253	0·99
	2·18	254	1·00
	2·94	258	1·01

	Concn.	*M.*	*a.*
o-Nitrobenzaldehydediphenylhydrazone (C_6H_6)	2·93	307	0·97
	4·36	309	0·97
	6·09	311	0·98
	7·88	313	0·99
m-Nitrobenzaldehydediphenylhydrazone (C_6H_6)	1·35	290	0·92
	3·51	307	0·97
	5·06	315	0·99
	7·31	320	1·01
p-Nitrobenzaldehydediphenylhydrazone (C_6H_6)	1·34	298	0·94
	3·83	311	0·98
	5·71	322	1·02
	7·46	326	1·03
	9·78	331	1·045

FIG. 3.

	Concn.	*M.*	*a.*
Acetophenonephenylhydrazone (C_6H_6). (See Fig. 1).			
Acetophenonediphenylhydrazone (C_6H_6)	1·61	272	0·95
	3·93	270	0·94
	6·49	271	0·95
	8·48	269	0·94

	Concn.	*M.*	*a.*
m-Nitroacetophenonephenylhydrazone ($C_6H_4Br_2$)	1·28	248	0·98
	2·51	259	1·02
	4·33	262	1·03
	6·06	280	1·10
	7·82	294	1·15
m-*Nitroacetophenonediphenylhydrazone* (C_6H_6)	1·28	307	0·93
	2·92	308	0·93
	4·43	311	0·94
	6·18	314	0·95
	7·69	312	0·94

FIG. 4.

	Concn.	*M.*	*a.*
Salicylidene-*p*-nitrophenylhydrazone ($C_{10}H_8$)	0·47	245	0·95
	1·17	258	1·005
	1·75	259	1·01
	2·83	264	1·03
	3·75	277	1·08

	Concn.	*M.*	*a.*
Salicylidene-*o*-nitrophenylhydrazone ($C_{10}H_8$)	1·56	239	0·93
	3·14	247	0·96
	6·05	257	1·00
	8·45	264	1·03

compounds in the presence of water also bear out these conclusions, that of salicylidene-*p*-nitrophenylhydrazone being 41°, and that of the *o*-isomer only 18°.

Evidence external to this investigation and in support of the conclusion reached is provided in the many recorded stable addition compounds formed between aromatic nitro-compounds and phenylhydrazones (Ciusa, *Gazzetta*, 1906, **36**, ii, 94; Ciusa and Agostinelli, *Atti R. Accad. Lincei*, 1906, **15**, ii, 238; 1907, **16**, i, 409; Sudborough and Beard, J., 1910, **97**, 773). The forces holding these components together are doubtless similar to those operating in the molecular association of the nitroarylhydrazones.

Because of the sparing solubility of the substances examined in this work, three different solvents were used for the cryosocopic measurements, *viz.*, benzene, naphthalene, and *p*-dibromobenzene. Certain anomalies were encountered in the use of naphthalene; *e.g.*, the three nitrobenzaldehydephenylhydrazones, though associated in *p*-dibromobenzene, were considerably less associated in naphthalene. This behaviour was eventually traced to compound formation between the solutes and naphthalene, tending thus to simplify the associated solute molecules. As it is not unusual for nitro-compounds to combine with naphthalene (see Pfeiffer, " Organische Molekülverbindungen," 2nd edn., 1927, p. 335 ff.), this solvent was finally abandoned, and *p*-dibromobenzene was used in its stead. Of the crysocopic measurements made in naphthalene and in *p*-dibromobenzene, only those of solutions which form a eutectic system are reported in this paper.

As in previous parts of this series, apparent molecular weights (M) and association factors (α) are deduced from the cryoscopic measurements according to the laws of ideal solutions. Conclusions as to molecular association are based, not on the absolute values of α, which may have no real significance, but rather on the slope of the association–concentration curves, a steep curve being interpreted as indicating a high degree of association, and a flat or gently sloped curve a low association. By comparing the slopes of these curves for substances of similar constitution, errors arising from departures from the ideal laws are very much diminished.

In the foregoing tables the solvents in which the measurements were made are given in parenthesis, and concentrations are expressed in g./100 g. of solvent. Figures in italics are calculated from the work of von Auwers, and, unless otherwise stated, are taken from von Auwers and Mann (*Ber.*, 1900, **33**, 1302).

EXPERIMENTAL.

Ordinary *p*-dibromobenzene (B.D.H.) was found to be pure enough for cryoscopic solvent use, repeated melting and partial freezing yielding a product with unaltered m. p.

m-*Nitroacetophenonediphenylhydrazone* was newly prepared; it formed bright yellow crystals from alcohol, m. p. 105° (Found: N, 12·7. $C_{20}H_{17}N_3O_2$ requires N, 12·7%).

The m. p. of benzaldehydephenylmethylhydrazone (106°) differs from that given in the literature (102°).

The following is a record of freezing-point systems showing compound formation:

*System naphthalene–*p-*nitrobenzaldehydephenylhydrazone.* Unstable compound (1 : 1 mol.), m. p. 123°, eutectic point for mixtures rich in naphthalene at 77°, and eutectic arrest for mixtures rich in hydrazone at 113°.

*System naphthalene–*m-*nitrobenzaldehydephenylhydrazone.* Unstable compound (1 : 1 mol.), m. p. 85°, eutectic point (40% by weight of naphthalene) at 67°.

Grateful acknowledgment is made to the Chemical Society for a grant, and to the Leicestershire Education Committee for a maintenance grant to one of us (J. A. M.).

UNIVERSITY COLLEGE, LEICESTER. [*Received, November 18th,* 1939.]