554. *The Associating Effect of the Hydrogen Atom. Part XIV. The Structure of Diacylamines and Related Substances.*

By Louis Hunter and Norman G. Reynolds.

Measurement of molecular weight of diacylamines, including acylsulphonyl- and disulphonylamines, by the cryoscopic method indicates a high degree of molecular association in these compounds, but on replacement of the imido-hydrogen atom the association is completely destroyed. The association of the former type is therefore attributed to intermolecular N–H–O bonds; and their tautomeric behaviour is held to be mesohydric (*i.e.*, due to the intermolecular sharing of the tautomeric hydrogen atom) rather than prototropic. Absence of the imidol form in these compounds is also supported by the properties of their metallic derivatives which, unlike those of the β-diketones, are typical non-chelate compounds.

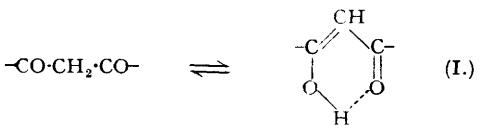
The main tenet of the conception of "mesohydric tautomerism" is the non-existence of individual tautomers in compounds exhibiting it. Such substances have been shown in previous parts of this series to possess an associated structure in which molecules are held together by intermolecular hydrogen bonds; it is assumed that the hydrogen atoms concerned are shared between adjacent molecules at the alternative sites customary in tautomeric change (Hunter, *J.*, 1945, 806). Crystallographic verification of this assumption is now beginning to accumulate; *e.g.*, acetamide (Senti and Harker, *J. Amer. Chem. Soc.*, 1940, **62**, 2008), acetanilide (Brown and Corbridge, *Nature*, 1948, **162**, 72), dicyandiamide (Hughes, *J. Amer. Chem. Soc.*, 1940, **62**, 1258), melamine (*idem*, *ibid.*, 1941, **63**, 1737), and the amino-pyrimidines (Clews and Cochran, *Acta Crystall.*, 1948, **1**, 4; 1949, **2**, 46) have all been shown to possess structures in which the molecules are juxtaposed in the crystal in such a way that the bonded hydrogen atom is shared between the alternative tautomeric sites in adjacent molecules. On the other hand, substances whose tautomeric behaviour depends on hydrogen attached to carbon, owing to the inability of the CH group to take part in stable hydrogen-bond formation, are non-associated and exist as individual tautomers interconvertible by a prototropic mechanism.

Acceptance of the theory of mesohydric tautomerism would therefore require the abandonment of the implications usually formulated as the reversible equilibrium $\cdot CO\cdot NH\cdot \rightleftharpoons \cdot C(OH){:}N\cdot$ in describing the tautomeric amide system, and of corresponding equilibria for all other mesohydric tautomeric systems. Support for this view is now sought in a comparison of compounds owing their tautomeric behaviour to the CH group (prototropic) with those owing it to the NH group (mesohydric). In particular, the β-diketones and the β-keto-esters (keto–enol type) will be compared with the diacylamines (amide–imidol type), and Table I compares the boiling points (at atmospheric pressure) of pairs of substances possessing on the one hand the group $\cdot CO\cdot CH_2\cdot CO\cdot$ and on the other the group $\cdot CO\cdot NH\cdot CO\cdot$, together with their methyl derivatives. It is noteworthy that, in spite of a difference of only one unit in formal molecular weight (expressed in parentheses), not only are the boiling points of the former type much lower than those of the latter, but the effect of methylating the tautomeric hydrogen atom is generally

TABLE I.

		B. p.			B. p.
$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$	(130)	181°	$CH_3{\cdot}CO{\cdot}NH{\cdot}CO_2Et$	(131)	205—215°
$CH_3{\cdot}CO{\cdot}CHMe{\cdot}CO_2Et$	(144)	186	$CH_3{\cdot}CO{\cdot}NMe{\cdot}CO_2Et$	(145)	189
$CH_3{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et$	(158)	185			
$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$	(100)	139	$CH_3{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CH_3$	(101)	223
$CH_3{\cdot}CO{\cdot}CHMe{\cdot}CO{\cdot}CH_3$	(114)	169	$CH_3{\cdot}CO{\cdot}NMe{\cdot}CO{\cdot}CH_3$	(115)	192
$CH_3{\cdot}CO{\cdot}CMe_2{\cdot}CO{\cdot}CH_3$	(128)	174			
$CO_2Et{\cdot}CH_2{\cdot}CO_2Et$	(160)	198	$CO_2Et{\cdot}NH{\cdot}CO_2Et$	(161)	226
$CO_2Et{\cdot}CHMe{\cdot}CO_2Et$	(174)	199			
$CO_2Et{\cdot}CMe_2{\cdot}CO_2Et$	(188)	196			

to raise the boiling points of the former type but substantially to lower those of the latter. These effects are in harmony with the conclusion that substances possessing the group ·CO·NH·CO· are associated by a hydrogen-bond mechanism, whilst those possessing the group ·CO·CH_2·CO· are not. The unimolecular character of the latter type has been demonstrated by von Auwers (*Z. physikal. Chem.*, 1893, **12**, 692; 1894, **15**, 33), and this together with the other physical and chemical properties of the β-diketones is in complete accord with their representation as the following equilibrium:



(I.)

Indeed, the quantitative assessment of this equilibrium and its mobility under the influence of catalysts have provided the very basis for the development of tautomeric theory in the last half-century. Nevertheless, in spite of the abundant proof of prototropy in the case of keto–enol systems, the representation of amides as an amide–imidol equilibrium rests on nothing more secure than an implied analogy. It is true, however, that extensive spectroscopic studies on amides have been made, but owing to the difficulty of interpretation of spectroscopic data the evidence is largely conflicting. Hantzsch (*Ber.*, 1931, **64**, 661) claimed that the ultra-violet absorption spectra of trichloroacetamide and benzamide point to a predominantly imidol structure in these amides, but Freymann and Freymann (*Compt. rend.*, 1936, **202**, 1850) found nothing in the infra-red absorption spectra of benzamide and other amides to correspond to the hydroxyl group. On the other hand, recent measurements of ultra-violet absorption of diacetylamine (Polya and Spotwood, *Rec. Trav. chim.*, 1949, **68**, 573) are interpreted as favouring an imidol–enol structure. A detailed examination of infra-red absorption of a large number of amides by Richards and Thompson (*J.*, 1947, 1248) indicated the absence of the C=N link and therefore of the imidol structure. Their conclusions favour the formal amide structure with intermolecular N–H–O bonds, a result which is in harmony with *X*-ray diffraction evidence for crystalline acetamide (Senti and Harker, *loc cit.*).

For the purpose of the present investigation, measurements of molecular weight of a large number of imido-compounds containing two acyl (or other electron-attracting) groups have been made, and the results indicate a high degree of molecular association in these compounds. Figs. 1—6 show the variation of the association factor (α) with concentration in nitrobenzene or benzene solution, molecular weights being measured cryoscopically. The choice of nitrobenzene as a cryoscopic solvent has been made necessary by the sparing solubility of many of the solutes; that such solutes continue to exhibit molecular association in this donor solvent is held to give additional support to the view that they possess a highly associated structure. As in previous parts of this series, molecular association is inferred in all cases in which the association factor increases substantially with rising concentration; *i.e.*, a steep association–concentration curve is taken to indicate molecular association, whereas a flat or gently sloped curve (in the region, $\alpha = 1$) is interpreted as indicating the absence of association. It will be seen from Fig. 1 (showing acylcarbamic esters, diacylamines, and dicarbalkoxyamines), Fig. 2 (showing acylsulphonamides), Fig. 3 (showing disulphonylamines), and Fig. 4 (showing acylthioncarbamic esters), that the compounds possessing an unsubstituted imido-group are all highly associated, but that substitution of the imido-hydrogen atom by alkyl or aryl groups causes complete suppression of molecular association. It would appear, then, that the molecular association of the former type is due to intermolecular hydrogen bonding (N–H–O) of

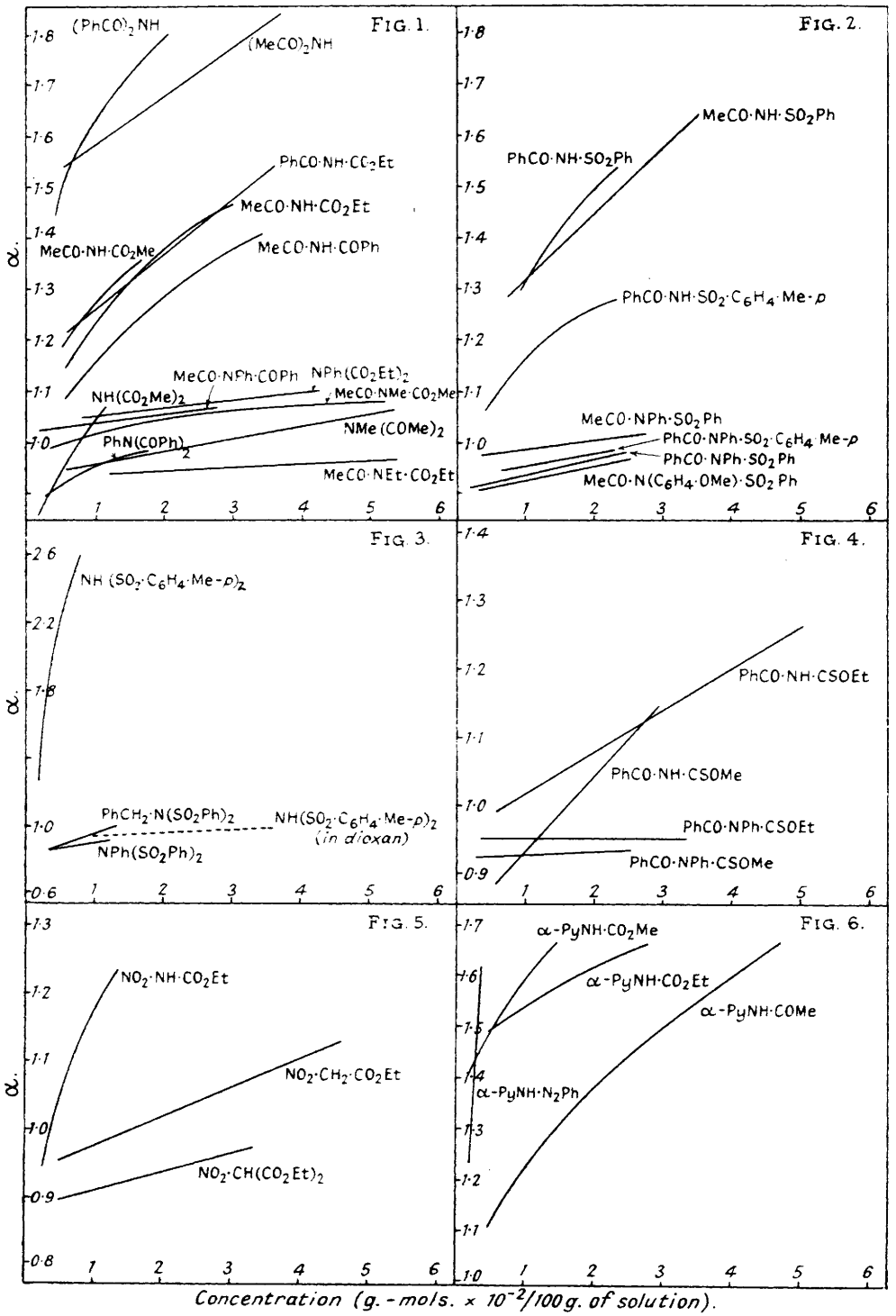


FIG. 1.
(PhCO)$_2$NH
(MeCO)$_2$NH
PhCO·NH·CO$_2$Et
MeCO·NH·CO$_2$Et
MeCO·NH·CO$_2$Me
MeCO·NH·COPh
MeCO·NPh·COPh
NPh(CO$_2$Et)$_2$
NH(CO$_2$Me)$_2$
MeCO·NMe·CO$_2$Me
NMe(COMe)$_2$
PhN(COPh)$_2$
MeCO·NEt·CO$_2$Et
FIG. 2.
MeCO·NH·SO$_2$Ph
PhCO·NH·SO$_2$Ph
PhCO·NH·SO$_2$·C$_6$H$_4$·Me-p
MeCO·NPh·SO$_2$Ph
PhCO·NPh·SO$_2$·C$_6$H$_4$·Me-p
PhCO·NPh·SO$_2$Ph
MeCO·N(C$_6$H$_4$·OMe)·SO$_2$Ph
FIG. 3.
NH(SO$_2$·C$_6$H$_4$·Me-p)$_2$
PhCH$_2$·N(SO$_2$Ph)$_2$
NH(SO$_2$·C$_6$H$_4$·Me-p)$_2$
(in dioxan)
NPh(SO$_2$Ph)$_2$
FIG. 4.
PhCO·NH·CSOEt
PhCO·NH·CSOMe
PhCO·NPh·CSOEt
PhCO·NPh·CSOMe
FIG. 5.
NO$_2$·NH·CO$_2$Et
NO$_2$·CH$_2$·CO$_2$Et
NO$_2$·CH(CO$_2$Et)$_2$
FIG. 6.
α-PyNH·CO$_2$Me
α-PyNH·CO$_2$Et
α-PyNH·COMe
α-PyNH·N$_2$Ph
α
Concentration (g.-mols. × 10^{-2}/100 g. of solution).

Fig. 1.

Concn.	*M.*	α.
NN-Dibenzoylamine.		
0·36	331	1·47
0·54	329	1·46
0·74	365	1·62
1·15	377	1·67
1·54	384	1·71
2·05	405	1·80

Concn.	*M.*	α.
NN-Diacetylamine.		
0·58	*156*	*1·55*
1·14	*161*	*1·59*
1·85	*169*	*1·67*
2·56	*172*	*1·71*
3·67	*185*	*1·83*

Concn.	*M.*	α.
Methyl acetylcarbamate.		
0·53	140	1·19
1·02	150	1·28
1·68	159	1·36

Concn.	*M.*	α.
Ethyl benzoylcarbamate.		
0·67	236	1·22
1·53	252	1·30
2·66	277	1·44
3·50	294	1·52

Ethyl acetylcarbamate.		
0·57	*150*	*1·14*
1·38	*171*	*1·30*
1·98	*182*	*1·38*
2·53	*187*	*1·43*
2·83	*190*	*1·45*

N-Benzoylacetamide.		
0·60	178	1·09
2·10	212	1·30
3·33	228	1·40

Dicarbomethoxyamine.		
0·16	106	0·80
0·47	126	0·95
0·81	134	1·00
1·06	140	1·05

NN-Dicarbethoxyaniline.		
0·91	249	1·05
1·77	252	1·07
2·80	254	1·07
3·62	259	1·09
4·20	261	1·10

N-Benzoylacetanilide.		
0·21	243	1·02
0·59	247	1·03
1·24	248	1·04
1·97	252	1·05
2·77	256	1·07

Methyl *N*-acetyl-*N*-methylcarbamate.		
0·45	129	0·99
1·26	136	1·04
2·06	134	1·03
3·66	140	1·07
5·10	142	1·08

NN-Dibenzoylaniline.		
0·37	269	0·90
1·26	292	0·97
1·81	295	0·98

NN-Diacetylmethylamine.		
0·64	*109*	*0·95*
1·85	*111*	*0·97*
3·51	*118*	*1·03*
4·09	*119*	*1·04*
5·39	*121*	*1·06*

Concn.	*M.*	α.
Ethyl *N*-acetyl-*N*-ethylcarbamate.		
1·32	*147*	*0·93*
3·42	*154*	*0·97*
4·48	*152*	*0·96*
5·37	*150*	*0·94*

Fig. 2.

Concn.	*M.*	α.
N-Benzoylbenzenesulphonamide.		
1·01	345	1·32
1·36	365	1·40
1·80	376	1·44
2·34	398	1·53

Concn.	*M.*	α.
N-Benzenesulphonylacetamide.		
0·81	257	1·29
1·48	275	1·38
2·05	286	1·44
2·80	306	1·54
3·47	323	1·63

Concn.	*M.*	α.
N-Benzoyltoluene-*p*-sulphonamide.		
0·54	294	1·07
0·89	322	1·17
1·41	331	1·20
1·87	342	1·25
2·26	353	1·28

Concn.	*M.*	α.
N-Benzenesulphonylacetanilide.		
0·46	267	0·97
1·16	273	0·99
2·47	279	1·01
2·78	279	1·01

N-Benzoyltoluene-*p*-sulphonanilide.		
0·72	333	0·95
1·12	333	0·95
1·79	340	0·97
2·22	346	0·99

N-Benzoylbenzenesulphonanilide.		
0·19	305	0·91
0·79	311	0·92
1·24	318	0·94
1·74	324	0·96
2·40	330	0·98

N-Benzenesulphonylacet-*p*-anisidide.		
0·43	277	0·91
0·90	276	0·91
1·33	289	0·95
1·79	286	0·94
2·48	297	0·97

Fig. 3.

Concn.	*M.*	α.
NN-Ditoluene-*p*-sulphonylamine.		
0·20	442	1·36
0·27	600	1·85
0·49	717	2·21
0·61	763	2·35
0·76	835	2·57
0·87	309	0·95
1·93	314	0·97
2·83	317	0·97
3·55	321	0·99

* In dioxan.

Concn.	*M.*	α.
NN-Dibenzenesulphonylbenzylamine.		
0·39	335	0·87
0·85	362	0·94
1·25	377	0·97

Concn.	*M.*	α.
NN-Dibenzenesulphonylaniline.		
0·46	323	0·87
0·71	333	0·89
1·19	346	0·93

Fig. 4.

Concn.	*M.*	α.	Concn.	*M.*	α.	Concn.	*M.*	α.	Concn.	*M.*	α.
Ethyl benzoylthion-carbamate.			Methyl benzoylthion-carbamate.			Methyl *N*-benzoyl-*N*-phenylthioncarbamate.			Ethyl *N*-benzoyl-*N*-phenylthioncarbamate.		
0·57	*211*	*1·01*	*0·58*	*169*	*0·87*	*0·33*	*250*	*0·92*	*0·41*	*271*	*0·95*
1·20	*212*	*1·01*	*1·16*	*183*	*0·94*	*1·47*	*252*	*0·93*	*1·13*	*270*	*0·95*
1·91	*223*	*1·07*	*1·65*	*195*	*1·00*	*2·54*	*252*	*0·93*	*1·96*	*271*	*0·95*
2·63	*233*	*1·11*	*2·49*	*211*	*1·08*				*2·62*	*272*	*0·95*
3·51	*245*	*1·17*	*2·92*	*221*	*1·14*				*3·26*	*272*	*0·95*
4·39	*255*	*1·22*									
5·01	*263*	*1·26*									

Fig. 5.

Concn.	*M.*	α.	Concn.	*M.*	α.	Concn.	*M.*	α.
Ethyl nitrocarbamate.			Ethyl nitroacetate.			Ethyl nitromalonate.		
0·20	*127*	*0·95*	*0·55*	*128*	*0·96*	*0·51*	*184*	*0·90*
0·47	*140*	*1·05*	*1·25*	*129*	*0·97*	*1·44*	*187*	*0·91*
0·78	*150*	*1·12*	*2·13*	*135*	*1·01*	*2·34*	*195*	*0·95*
1·05	*156*	*1·17*	*3·54*	*144*	*1·08*	*3·28*	*199*	*0·97*
1·29	*164*	*1·23*	*4·66*	*150*	*1·13*			

Fig. 6.

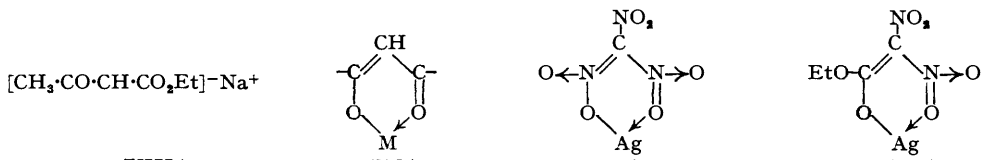
Concn.	*M.*	α.	Concn.	*M.*	α.	Concn.	*M.*	α.	Concn.	*M.*	α.
2-Phenyldiazo-aminopyridine.			Methyl 2-pyridyl-carbamate.			Ethyl 2-pyridyl-carbamate.			2-Acetamido-pyridine.		
0·18	*245*	*1·24*	*0·25*	*216*	*1·42*	*0·49*	*236*	*1·49*	*0·43*	*151*	*1·11*
0·24	*291*	*1·47*	*0·66*	*237*	*1·56*	*1·23*	*258*	*1·56*	*1·29*	*175*	*1·28*
0·28	*318*	*1·60*	*1·16*	*242*	*1·59*	*2·13*	*268*	*1·61*	*2·31*	*192*	*1·41*
			1·40	*253*	*1·66*	*2·81*	*276*	*1·66*	*3·21*	*204*	*1·50*
									4·70	***226***	***1·66***

a kind similar to that suggested for amides and sulphonamides (Chaplin and Hunter, *J.*, **1937**, 1114). Such a structure is inconsistent with the formation of an imidol, which, by analogy with the enol (I), would be expected to assume the chelate ring structure (II), and thus to show non-associating behaviour. Similar associated character is revealed in ethyl nitrocarbamate, which is compared (Fig. 5) with the unassociated nitroacetate and nitromalonate; and Fig. 6 illustrates the high degree of association in the acyl-, carbalkoxy-, and aryldiazo-derivatives of 2-aminopyridine. The molecular association of all these compounds indicates that they possess *intermolecular* N–H–O or N–H–N bonds, structures completely at variance with the chelate ring structures (V), (VI), and (VII).

A list of the diacylamines and related substances on which measurements have been made is shown in Table II; in the third column are indicated the hypothetical tautomers which would result from prototropic change, all of which, by virtue of their co-ordinated hydroxyl groups, would be expected to be non-associated.

In spite of the highly associated character of the substances listed in Table II it could be argued that this is no proof of the absence in such systems of the imidol form, which, if present in small amounts, would have little effect on the degree of association measured in solution. To meet this valid point a comparison has been made between the metallic derivatives of some diacylamines and those derived from certain prototropic systems.

(1) *Metallic Derivatives of Prototropic Systems.*—Prototropic systems in which at least one tautomer is acidic yield metallic derivatives, of which by far the greatest number of examples are provided by the β-diketones and the β-keto-esters. Those containing alkali metals are

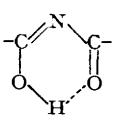
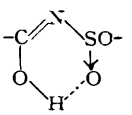
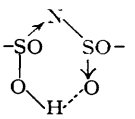
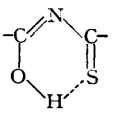
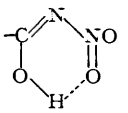
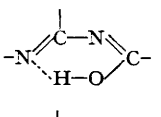
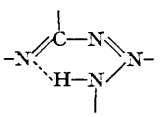


(VIII.) (IX.) (X.) (XI.)

clearly electrovalent salts (*e.g.*, ethyl sodioacetoacetate, VIII), but those derived from metals of high co-ordinative capacity possess properties indicating a structure (IX; M = 1 equiv. of

metal) in which the metal is covalently attached to the two keto-oxygen atoms (Morgan and Moss, *J.*, 1913, **103**, 78; 1914, **105**, 189), a structure which receives support from *X*-ray diffraction evidence (Cox and Webster, *J.*, 1935, 731). Such chelate metallic compounds are derived from and are structurally closely related to the enol (I), and this is doubtless the origin of the ferric chloride colour test for enols. By virtue of the lack of ionic character in the metal M, these derivatives are only sparingly soluble in water, are frequently soluble in organic solvents, and often possess high colour, usually quite different from that of the metallic ion.

TABLE II.

	Imido-compound.	Structural group.	Hypothetical tautomer	
Fig. 1.	Acylcarbamic esters, $R\cdot CO\cdot NH\cdot CO_2R$ Diacylamines, $R\cdot CO\cdot NH\cdot COR$ Dicarbalkoxyamines, $CO_2R\cdot NH\cdot CO_2R$	$\cdot CO\cdot NH\cdot CO\cdot$		(II.)
Fig. 2.	Acylsulphonylamines, $R\cdot SO_2\cdot NH\cdot COR$	$\cdot CO\cdot NH\cdot SO_2\cdot$		(III.)
Fig. 3.	Disulphonylamines, $R\cdot SO_2\cdot NH\cdot SO_2R$	$\cdot SO_2\cdot NH\cdot SO_2\cdot$		(IV.)*
Fig. 4.	Acylthioncarbamic esters, $R\cdot CO\cdot NH\cdot CS\cdot OR$	$\cdot CO\cdot NH\cdot CS\cdot$		
Fig. 5.	Nitrocarbamic esters, $NO_2\cdot NH\cdot CO_2R$	$\cdot CO\cdot NH\cdot NO_2$		(V.)
Fig. 6.	2-Acylamidopyridines, $C_5H_4N\cdot NH\cdot COR$ 2-Pyridylcarbamic esters, $C_5H_4N\cdot NH\cdot CO_2R$	$\cdot N{:}C\cdot NH\cdot CO\cdot$		(VI.)
	2-Aryldiazoaminopyridines, $C_5H_4N\cdot NH\cdot N{:}NR$	$\cdot N{:}C\cdot NH\cdot N{:}N\cdot$		(VII.)

* Recent work on the structure of the sulphone group favours double rather than co-ordinate bonds in these formulæ.

Metallic derivatives of other prototropic systems of similar types are illustrated by silver nitroform (X) (Sidgwick's "Organic Chemistry of Nitrogen," Taylor and Baker, 1942, p. 246) and the silver salt of ethyl dinitroacetate (XI).

(2) *Metallic Derivatives of Diacylamines.*—In spite of being stronger acids than the β-diketones, the diacylamines form less stable derivatives with metals. Those derived from the alkali metals are strongly hydrolysed by water and are frequently only obtainable under anhydrous conditions; they clearly possess the electrovalent structure (XII). By double decomposition of the sodium derivatives with other metallic salts a few heavy-metal derivatives have been described, such as silver (Barth and Senhofer, *Ber.*, 1876, **9**, 977) and cupric dibenzoylamine (XIII) (Ley and Werner, *ibid.*, 1913, **46**, 4049). The properties of these derivatives suggest a structure similar to that of the sodium salt (XII). For example, the cupric compound (dihydrate) is blue-grey in colour and is fairly easily hydrolysed; it has none of the properties usually associated with co-ordinated copper, and is best represented as (XIII) rather than as a derivative of (II).

In the present investigation only those diacylamines having one or two arylsulphonyl groups have proved sufficiently acidic to yield salts stable enough to be characterised. Some

$[R{\cdot}CO{\cdot}N{\cdot}COR]^{-}Na^{+}$ (XII.) $[Ph{\cdot}CO{\cdot}N{\cdot}COPh]^{-}{}_2Cu^{++},2H_2O$ (XIII.) $CH_3{\cdot}CO{\cdot}NH{\cdot}SO_2{\cdot}C_7H_7$-*p* (XIV.)

$(p\text{-}C_7H_7{\cdot}SO_2)_2NH$ (XV.) $Ph{\cdot}CO{\cdot}NH{\cdot}SO_2Ph$ (XVI.) $[CH_3{\cdot}CO{\cdot}N{\cdot}SO_2{\cdot}C_7H_7\text{-}p]^{-}{}_2Co^{++},6H_2O$ (XVII.)

twelve metallic salts have been isolated as hydrates, ammines, or in the anhydrous condition from *N*-toluene-*p*-sulphonylacetamide (XIV), *NN*-ditoluene-*p*-sulphonylamine (XV), and *N*-benzoylbenzenesulphonamide (XVI). They prove to be water-soluble crystalline substances, sparingly or not at all soluble in organic solvents, with colours characteristic of the metallic ion they possess. On being heated, they decompose without true melting, although the highly hydrated salts appear to dissolve in their water of hydration. They are therefore judged to have structures in which the metal is electrovalently attached, as in cobaltous *N*-toluene-*p*-sulphonylacetamide hexahydrate (XVII), and structures such as (III) and (IV) (H = metal) for these derivatives are completely untenable. It is doubtless on this account that amides and diacylamines fail to give the ferric chloride colour test.

Experimental.

(The analytical data given below for water of hydration do not always conform to those required owing to the difficulty of dehydrating these acylated compounds without causing hydrolysis.)

Metallic Salts of N-*Toluene*-p-*sulphonylacetamide*.—These were prepared, unless otherwise stated, by the action of the appropriate carbonate on an aqueous alcoholic solution of the above. The *lithium* salt monohydrate formed white rectangular plates, readily soluble in water, alcohol, and acetone, insoluble in other organic solvents or in moist toluene (Found: N, 5·8; Li, 2·8; loss at 100°, 9·3. $C_9H_{10}O_3NSLi,H_2O$ requires N, 5·9; Li, 2·9; H_2O, 7·6%). The *sodium* salt monohydrate formed white crystals from water (Found: N, 5·5; Na, 8·9; loss at 100°, 7·9. $C_9H_{10}O_3NSNa,H_2O$ requires N, 5·5; Na, 9·1; H_2O, 7·1%). The *diamminocupric* salt was obtained as royal-blue crystals on mixing equivalent weights of copper sulphate and toluene-*p*-sulphonylacetamide in concentrated aqueous ammonia. It was insoluble in water and in organic solvents, and was stable in a vacuum-desiccator over sulphuric acid (Found: total N, 10·5; NH_3, 6·4. $C_{18}H_{20}O_6N_2S_2Cu,2NH_3$ requires total N, 10·7; NH_3, 6·5%). Attempts to prepare a copper derivative in the absence of ammonia yielded only basic compounds.

The *barium* salt monohydrate formed white needles, moderately soluble in water, insoluble in organic solvents (Found: N, 4·8; Ba, 23·7; loss at 100°, 3·1. $C_{18}H_{20}O_6N_2S_2Ba,H_2O$ requires N, 4·8; Ba, 23·7; H_2O, 3·1%). The *cobaltous* salt hexahydrate formed pink hexagonal plates from water (Found: N, 4·5; Co, 9·95; loss at 100°, 18·8. $C_{18}H_{20}O_6N_2S_2Co,6H_2O$ requires N, 4·7; Co, 10·0; H_2O, 18·3%), yielding a blue anhydrous salt which reverted to pink in water. The *nickel* salt nonahydrate formed green rhombs from water [Found: N, 4·4; Ni, 9·1; loss over H_2SO_4 (vac.), 20·4. $C_{18}H_{20}O_6N_2S_2Ni,9H_2O$ requires N, 4·3; Ni, 9·1; H_2O, 25·1%]. The *manganous* salt nonahydrate was obtained by double decomposition of the sodium salt with manganese sulphate as cream-coloured rhombs from water (Found: N, 4·3; Mn, 8·5; loss at 100°, 25·2. $C_{18}H_{20}O_6N_2S_2Mn,9H_2O$ requires N, 4·4; Mn, 8·6; H_2O, 25·3%). A ferrous salt was obtained as pale green plates rapidly becoming brown, insoluble in organic solvents, and was not analysed.

Metallic Salts of NN-*Ditoluene*-p-*sulphonylamine*.—The amine, m. p. 174° (Found: N, 4·2. Calc.: N, 4·3%), was treated in aqueous alcoholic solution with the appropriate metallic carbonate. The *cupric* salt dodecahydrate formed pale blue needles from water (Found: Cu, 6·8; loss at 100°, 23·0. $C_{28}H_{28}O_8N_2S_4Cu,12H_2O$ requires Cu, 6·8; H_2O, 23·3%). The *barium* salt monohydrate formed white needles from water (Found: Ba, 16·9; loss at 100°, 2·3. $C_{28}H_{28}O_8N_2S_4Ba,H_2O$ requires Ba, 17·1; H_2O, 2·2%). The *nickel* salt 13-hydrate formed green rhombs from water [Found: N, 3·0; Ni, 6·2; loss over P_2O_5 (vac.), 19·2. $C_{28}H_{28}O_8N_2S_4Ni,13H_2O$ requires N, 3·0; Ni, 6·2; H_2O 24·8%]; in addition to being readily soluble in water, it was sufficiently soluble to impart a green colour to alcohol, acetone, chloroform, and pyridine.

Metallic Salts of N-*Benzoylbenzenesulphonamide*.—This substance was sufficiently acid to decompose many metallic carbonates, but the resulting salts were seldom isolated in a pure condition owing to more or less extensive hydrolysis; *e.g.*, nickel and cobalt carbonates yielded green and pink solutions, respectively, but the resulting filtrates rapidly hydrolysed. The *potassium* salt formed white feathery crystals, very soluble in water (Found: K, 12·7. $C_{13}H_{10}O_3NSK$ requires K, 13·0%), and the *tetramminocupric* salt, prepared by mixing equivalent amounts of copper sulphate and *N*-benzoylbenzenesulphonamide in concentrated aqueous ammonia, formed royal-blue crystals (Found: total N, 12·4; Cu, 9·8; NH_3, 9·9. $C_{26}H_{20}O_6N_2S_2Cu,4NH_3$ requires total N, 12·9; Cu, 9·8; NH_3, 10·0%). It was hydrolysed by water, giving a blue solution and a white precipitate.

The following new compounds were prepared for molecular-weight measurements in the course of this work: *methyl* N-*acetyl*-N-*methylcarbamate*, b. p. 174—176° (Found: N, 10·4. $C_5H_9O_3N$ requires N, 10·7%), and *ethyl* N-*acetyl*-N-*ethylcarbamate*, b. p. 191—192° (Found: N, 8·65. $C_7H_{13}O_3N$ requires N, 8·8%), both colourless liquids of peppermint odour; N-*benzenesulphonylacet*-p-*anisidide*, white crystalline solid (from alcohol), m. p. 142° (Found: N, 4·5. $C_{15}H_{15}O_4NS$ requires N, 4·6%). *Methyl*

2-*pyridylcarbamate* formed white crystals (from alcohol), m.p. 130° (Found: N, 18·3. $C_7H_8O_2N_2$ requires N, 18·4%).

Molecular-weight Data.—Molecular weights were measured cryoscopically, the majority in nitrobenzene solution, but those recorded in italics in benzene solution. In the tables, concentrations are expressed as g.-mols.($\times 10^2$)/100 g. of solution; M is the apparent molecular weight deduced according to ideal-solution laws; the association factor (a) is calculated as the ratio of M to the formula weight. The extremely steep curve for *NN*-ditoluene-*p*-sulphonylamine (Fig. 3) in nitrobenzene solution calls for comment. Although the values for a may have no absolute significance, that the substance is substantially associated is indicated by the flatness of the curve for this substance in dioxan solution (Fig. 3), indicating a complete loss of association in the latter solvent.

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