165. *The Associating Effect of the Hydrogen Atom. Part XII. The* N–H–N *Bond. The Structure and Tautomerism of Cyanamides.*

By L. Hunter and H. A. Rees.

Examination of the physical properties and measurement of the molecular weight of cyanamide and its organic derivatives show that they are of two distinct types: those possessing an unsubstituted imino-group ($NH_2\cdot CN$ and $NHR\cdot CN$) are highly associated in benzene and in naphthalene solution, whereas those in which both amino-hydrogen atoms are replaced ($NRR'\cdot CN$) are unimolecular. The molecular association of the former type, as well as their tautomeric character, is attributed to N–H–N bonds between adjacent molecules. Cyanamide and its monosubstituted derivatives therefore provide further examples of mesohydric tautomerism (Hunter, *Chem. and Ind.*, 1941, **60**, 32).

The physical properties of cyanamide are strongly suggestive of a highly associated molecular structure. For example, in spite of its low molecular weight, cyanamide has a boiling point far above that of all other simple cyano-derivatives (Table I); that this is probably a consequence of a hydrogen-bond structure is revealed in Table II, from which it is evident that the large fall in boiling point on passing from cyanamide to its dialkyl derivatives is compensated for by rising molecular weight only on reaching the diamyl derivative, whose molecular weight is more than four times that of cyanamide.

Table I.*

	B. p.		B. p.
Cyanamide (42)	140°/19 mm.	Cyanogen chloride (61·5)	12°
Hydrogen cyanide (27)	26	Cyanogen bromide (106)	61
Acetonitrile (41)	82	Methyl thiocyanate (73)	131
Cyanogen (52)	−21	Methyl cyanoformate (85)	101
Acetyl cyanide (69)	93		

Table II.*

Cyanamide (42)	140°/19 mm.	Dipropylcyanamide (126)	104°/18 mm.
Dimethylcyanamide (70)	52/14 mm.	Dibutylcyanamide (154)	147—151/35 mm.
Diethylcyanamide (98)	68/10 mm.	Di*iso*amylcyanamide (182)	144/20 mm.
Diallylcyanamide (122)	105—110/18 mm.		

Solubility considerations provide further indications of a hydrogen-bond structure: cyanamide shows a high solubility in water and all other donor solvents, but is only very sparingly soluble in benzene, naphthalene, chloroform, petrol, carbon disulphide, etc.

In chemical properties also, there is good evidence for regarding cyanamide as a substance in tautomeric equilibrium, *i.e.*, $NH_2\cdot CN \rightleftharpoons NH{:}C{:}NH$. This has a close formal resemblance to amidine tautomerism, and the tautomeric behaviour of amidines has already been correlated (Hunter and Marriott, J., 1941, 777) with their associated (hydrogen-bond) structure. To determine whether a similar correlation prevails in the cyanamides, measurements of molecular weight have now been made on cyanamide (I) and its mono-(II) and di-(III) substituted derivatives. The results (Fig. 1) clearly divide cyanamides into two classes; those possessing an unsubstituted imino-group (I and II; curves 1—5) are markedly associated, whereas those in which there is no free hydrogen atom (III; R′ = alkyl, aryl, or acyl; curves 6—11) are substantially unimolecular. Since this subdivision is in harmony with the presence of tautomerism in the former type (I and II) and its absence in the latter (III), it seems clear that cyanamides of the former class owe their associated character no less than their tautomeric behaviour to molecular union through hydrogen bonds (N–H–N), the imino-hydrogen atom of one molecule being shared with the cyano-nitrogen atom of a second.

$NH_2\cdot CN$	$NHR\cdot CN$	$NRR'\cdot CN$	$NHAr\cdot CH_2\cdot CN$	$NArAc\cdot CH_2\cdot CN$
(I.)	(II.)	(III.)	(IV.)	(V.)

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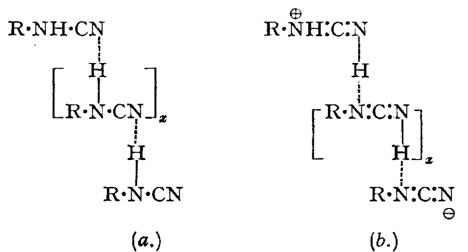
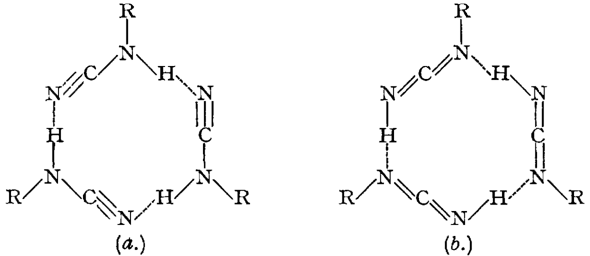
* Formal molecular weights in parentheses.

The molecular-weight determinations now recorded were made cryoscopically in benzene or naphthalene over a range of concentration. As in previous parts of this series, molecular association is inferred from the molecular-weight measurements in all cases in which the factor of association (α) 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 absence of association. Cyanamide itself was too insoluble in benzene or naphthalene to give reliable results, and was measured cryoscopically in nitrobenzene solution. In spite of the donor character of this solvent, and its consequent tendency to simplify the solute molecules, a 2% solution of cyanamide therein showed an association factor of well over 2·0. On the other hand, in aqueous solution cyanamide is unimolecular, indicating that in this solvent its intermolecular hydrogen bonds are probably superseded by bonds (N–H–O) with the solvent water molecules.

Except that intermolecular bonding is through hydrogen, no conclusions can be drawn from the molecular-weight evidence as to the type of associated molecules present in (I) and (II), for the molecular weight–concentration curves show little or no falling off in slope with increasing concentration. This may indicate chain polymers, and the hydrogen bond being regarded as a resonance phenomenon, a chain polymer of the cyanamide (II) containing $x + 2$ molecules is depicted in (VI), in which (*a*) and (*b*) are the unperturbed forms of the resonance hybrid. Cyclic polymers are not excluded, and due weight being given to the rectilinear disposition of the N–C–N skeleton in cyanamides, a practically strainless trimer (VII) can be constructed involving no separation of charges in the unperturbed forms (*a*) and (*b*).


(*a*.) (*b*.)

(VI.)

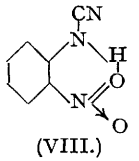

(*a*.) (*b*.)

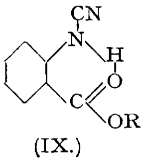
(VII.)

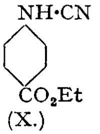
The close connexion between hydrogen-bond association in the cyanamides and their tautomeric character is strikingly demonstrated by a comparison of arylcyanamides (II; R = aryl) with their homologous arylaminoacetonitriles (IV), in which the imino- and the cyano-groups are separated by a methylene group. Not only are substances of the latter type devoid of tautomeric character, but their molecular association (Fig. 2) is very markedly reduced in comparison with that of the cyanamides, in spite of the presence in their molecules of the associating groups imino- and cyano-. That the small though noticeable amount of molecular association shown by the arylaminoacetonitriles can scarcely be due to hydrogen-bond association is shown by the fact that p-*tolylacetamidoacetonitrile* (V; Ar = *p*-tolyl), in which the imino-hydrogen atom has been replaced by acetyl, shows only slightly less association than its parent imine (IV; Ar = *p*-tolyl).

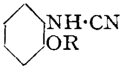
This predisposition on the part of tautomeric hydrogen to engage in hydrogen-bond formation has frequently been noted in previous parts of this series; *e.g.*, comparison between amides and imino-ethers (J., 1937, 1114), pyrazoles and pyrazolines (J., 1941, 3), thioacridone and thiodiphenylamine (J., 1942, 640).

In addition to cyanamides of types (II) and (III), it was considered of interest to examine a few arylcyanamides possessing *o*-substituent groups capable of achieving chelate ring formation with the hydrogen atom of the cyanamido-group. Fig. 3 compares phenylcyanamide (II; R = Ph) with *o*-nitro- (VIII; curve 16) and *o*-carbalkoxy-phenylcyanamides (IX; curves 17 and 18), and the greatly reduced molecular association in the latter points to a large proportion of their molecules possessing intramolecular hydrogen bonds (N–H–O) as indicated. This is supported by the fact that p-*carbethoxyphenylcyanamide* (X; curve 15), in which chelate ring formation is impossible, exhibits a higher degree of molecular association than its *o*-isomer (IX; R = Et; curve 18).


(VIII.)


(IX.)


(X.)

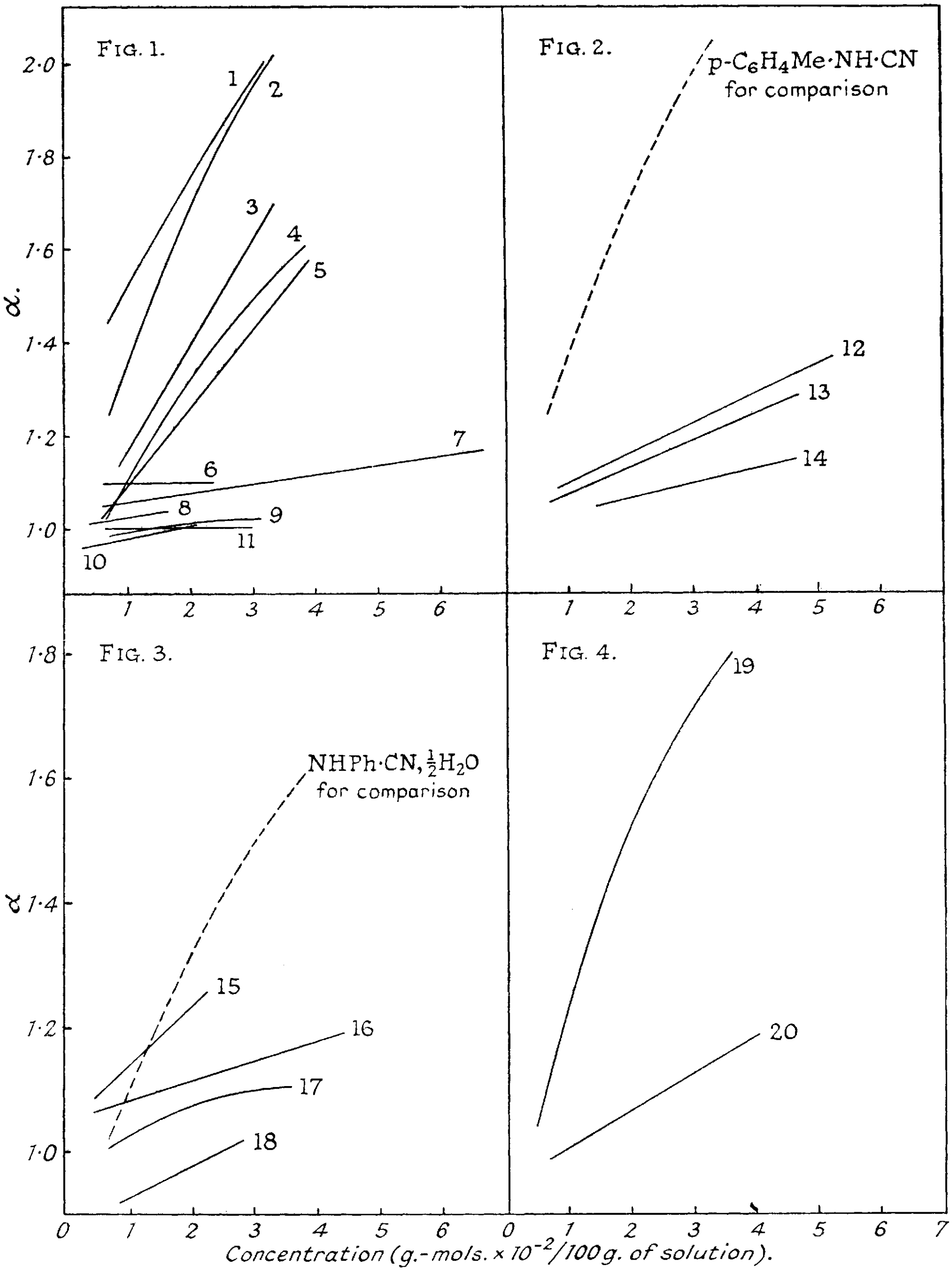

(XI.)

$NH:C(NH_2)\cdot NH\cdot CN$

(XII.)

A similar effect is noticeable in the *o*-alkoxyphenylcyanamides (XI), which, in comparison with their *p*-isomers, show a reduced degree of association (Figs. 1 and 4). It is doubtful whether this effect is due to chelate ring formation, as this would involve the very rare five-membered system. As the ethoxy-group produces a much larger effect than methoxy-, we are inclined to ascribe the effect to steric causes, especially as similar results (unpublished) have recently been obtained with *o*-substituted phenylurethanes in circumstances where no chelation is possible.

The above conclusions as to the structure of cyanamide can reasonably be extended to include its polymeride dicyandiamide, whose high melting point (209°) and low solubility in organic solvents indicate a high state of molecular association; for in the structure (XII) usually ascribed to this compound there are two groups contributing to hydrogen-bond association, *viz.*, the guanidino- (Hunter and Marriott, *loc. cit.*, p. 782) and the cyanamido-group. The cyclic trimer, melamine, is probably similarly complex. *X*-Ray analyses



of crystalline dicyandiamide (Hughes, *J. Amer. Chem. Soc.*, 1940, **62**, 1258) and of melamine (*ibid.*, 1941, **63**, 1737) are completely in harmony with this view.

EXPERIMENTAL.

The tendency of cyanamides to undergo *chemical* polymerisation (self-addition) to form substances of the melamine type has been kept constantly in mind throughout this work, for the formation of such products in the course of molecular-weight determinations would completely invalidate the conclusions. Two checks against this behaviour have been performed. Firstly, in most cases the cyanamide was recovered unchanged from the cryoscopic solvent at the conclusion of each series of molecular-weight measurements. Secondly, if the molecules exist in solution as aggregates linked by hydrogen bonds the reaction $(\text{NHR·CN})_x \rightleftharpoons x\text{NHR·CN}$ is readily reversible, the position of equilibrium depending on the concentration of the solution. Consequently, a set of cryoscopic measurements made on this solute at progressively increasing concentrations should give an association–concentration curve which is substantially reproducible when the same solution is progressively diluted with solvent. On the other hand, if the rising molecular weight were due to the (irreversible) formation of melamines, no such reproducibility would be expected, and the molecular weight would remain high after dilution. The application of both these checks left no doubt that melamines were not formed, in the experimental conditions used, by any of the compounds examined.

The behaviour of phenylcyanamide semihydrate is noteworthy, for there is reason to believe that the anhydrous compound has no real existence, it being immediately transformed into the tripolymer, triphenylmelamine. On drying the hydrate in a desiccator it rapidly liquefies and finally sets to a vitreous mass of triphenylmelamine. The hydrate is stable under moist conditions; it can therefore be kept unchanged in the open for very long periods in the winter months, but in dry weather it loses water and polymerises. It is for this reason that measurements were made (Fig. 1, curve 4) on the hydrate.

Revised m. p.'s are recorded for the following cyanamides: *p*-tolylcyanamide, m. p. 71—72° (lit., 69°); *N*-benzoylphenylcyanamide, m. p. 127° (lit., 118°) (Found: N, 12·8. Calc.: N, 12·6%); *N*-benzoyl-*p*-tolylcyanamide, m. p. 132° (lit., 126°); *o*-ethoxyphenylcyanamide, m. p. 103° (lit., 94°); *p*-ethoxyphenylcyanamide, m. p. 92° (lit., 87°); *o*-carbomethoxyphenylcyanamide, m. p. *111*° (lit., 105°); *o*-carbethoxyphenylcyanamide, m. p. 98° (lit., 94°); *o*-nitrophenylcyanamide, m. p. 155—156° (lit., 152°).

The following new compounds were prepared. N-*Benzoyl*-o-*tolylcyanamide*, white needles from aqueous alcohol, m. p. 95° (Found: N, 11·7. $C_{15}H_{12}ON_2$ requires N, 11·9%). o-*Methoxyphenylcyanamide*, white platelets from aqueous alcohol, m. p. 82° (Found: N, 19·0. $C_8H_8ON_2$ requires N, 18·9%). p-*Methoxyphenylcyanamide* gave evidence of dimorphism. The crude product, precipitated from sodium hydroxide solution by dilute acetic acid, was a microcrystalline, white powder melting unsharply about 80°. When recrystallised from water it yielded white prisms, m. p. 90—91°, but from alcohol it gave white plates, m. p. 75° (unsharp). By treating the alcoholic solution with seeds of the higher m. p. material, white prisms, m. p. 91°, were obtained. All specimens, whether of high or low m. p., crystallised from water in white prisms, m. p. 91° (Found: N, 19·0. $C_8H_8ON_2$ requires N, 18·9%).

p-*Methoxyphenyl*-N-*carbethoxycyanamide*. To a cold solution of the above compound (1 mol.) in pyridine was slowly added ethyl chloroformate (1 mol.), and the resulting solution was poured into dilute acid. The white precipitate was washed free from acid and crystallised while still moist from aqueous alcohol. It formed long white needles, m. p. 55° (Found: N, 12·9. $C_{11}H_{12}O_3N_2$ requires N, 12·7%).

p-*Carbethoxyphenylcyanamide*, white micro-crystals from aqueous alcohol, m. p. 151—152° (Found: N, 14·6. $C_{10}H_{10}O_2N_2$ requires N, 14·7%). p-*Tolylacetamidoacetonitrile*, stout white prisms from alcohol, m. p. 73° (Found: N, 15·0. $C_{11}H_{12}ON_2$ requires N, 14·9%).

Molecular-weight Data.—Molecular weights were measured cryoscopically in naphthalene solution, and, in the exceptions noted, in benzene solution. In the following tables, concentrations are expressed as g.-mols. × 10^{-2}/100 g. of solution, the formula weights appearing in parentheses; *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.

FIG. 1.

1. *o*-Tolylcyanamide (132).*

Concn.	*M*.	*a*.
0·67	190	1·44
1·12	205	1·55
2·20	236	1·79
3·14	263	2·00

2. *p*-Tolylcyanamide (132).*

Concn.	*M*.	*a*.
0·67	163	1·24
1·34	196	1·48
2·13	226	1·71
2·74	250	1·89
3·29	270	2·05

3. *p*-Methoxyphenylcyanamide (148).

Concn.	*M*.	*a*.
0·77	172	1·16
1·84	188	1·27
2·24	201	1·36
2·98	239	1·61
3·31	252	1·70

4. Phenylcyanamide semihydrate (127).

Concn.	*M*.	*a*.
0·65	129	1·02
1·52	149	1·17
2·19	175	1·38
2·87	189	1·48
3·73	203	1·60

5. *o*-Methoxyphenylcyanamide (148).*

Concn.	*M*.	*a*.
0·62	153	1·03
1·39	177	1·20
1·98	189	1·28
2·63	196	1·32
3·19	216	1·46
3·84	234	1·58

6. *N*-Benzoyl-*o*-tolylcyanamide (236).*

Concn.	*M*.	*a*.
0·52	266	1·13
1·12	260	1·10
1·70	248	1·05
2·35	260	1·10

7. Phenylmethylcyanamide (132).*

Concn.	*M*.	*a*.
0·65	139	1·05
2·18	144	1·09
3·25	144	1·09
5·25	152	1·15
6·66	155	1·17

8. *N*-Benzoyl-*p*-tolylcyanamide (236).*

Concn.	*M*.	*a*.
0·38	239	1·01
0·93	240	1·02
1·59	246	1·04

9. Diphenylcyanamide (194).

Concn.	*M*.	*a*.
0·81	189	0·97
1·35	197	1·02
2·00	196	1·01
2·78	199	1·03
3·16	193	1·00

10. *N*-Benzoylphenylcyanamide (222).*

Concn.	*M*.	*a*.
0·26	211	0·95
0·48	211	0·95
0·78	218	0·98
1·32	223	1·01
1·63	225	1·01
1·98	223	1·01

11. *p*-Methoxyphenyl-*N*-carbethoxycyanamide (220).

Concn.	*M*.	*a*.
0·63	223	1·01
1·25	222	1·00
2·09	222	1·00
2·93	220	1·00

FIG. 2.

12. Phenylaminoacetonitrile (132).*

Concn.	*M*.	*a*.
0·96	143	1·09
1·80	150	1·13
3·21	165	1·25
3·93	171	1·29
5·23	181	1·37

13. *p*-Tolylaminoacetonitrile (146).*

Concn.	*M*.	*a*.
0·79	155	1·06
1·65	162	1·11
2·29	167	1·14
3·52	179	1·23
4·71	189	1·29

14. *p*-Tolylacetamidoacetonitrile (188).

Concn.	*M*.	*a*.
1·54	197	1·04
2·96	207	1·10
4·14	211	1·13
4·65	215	1·15

FIG. 3.

15. *p*-Carbethoxyphenylcyanamide (190)

0·49	207	1·09
0·86	213	1·12
1·83	227	1·20
2·20	239	1·26

16. *o*-Nitrophenylcyanamide (163).

0·46	175	1·07
0·96	176	1·08
1·56	181	1·10
2·45	186	1·14
3·62	185	1·14
4·42	194	1·19

17. *o*-Carbmethoxyphenylcyanamide (176).

0·70	177	1·00
1·32	182	1·03
1·92	187	1·06
2·43	192	1·09
3·19	194	1·10
3·57	193	1·10

18. *o*-Carbethoxyphenylcyanamide (190).

0·82	174	0·92
1·57	178	0·94
2·17	185	0·98
2·83	194	1·02

FIG. 4.

19. *p*-Ethoxyphenylcyanamide (162).

0·41	170	1·05
0·95	182	1·12
1·42	203	1·25
1·77	246	1·52
2·21	256	1·58
2·43	277	1·71
3·64	290	1·79

20. *o*-Ethoxyphenylcyanamide (162).

0·67	160	0·99
2·03	174	1·07
2·87	182	1·12
3·64	190	1·17
4·03	193·5	1·19

Molecular weight of cyanamide (42) *in nitrobenzene.*

2·64	77	1·83
5·11	97	2·31

* In benzene solution.

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