172. *The Associating Effect of the Hydrogen Atom. Part XIII. The* N–H–O *Bond. Esters of Carbamic Acid.*

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Measurements of the molecular weight of esters of carbamic acid reveal a high degree of molecular association in those esters possessing one or more unsubstituted imino-hydrogen atoms (I and II), whereas those in which both hydrogen atoms are replaced (III) are non-associated. This, as well as their tautomeric character, is attributed to a hydrogen-bond (N–H–O) structure in the former. Further measurements indicate that esters of carbanilic acid (VIII) can suffer a diminution of molecular association by reason of the following three causes: (*a*) co-ordination of the imino-hydrogen atom with suitable *ortho*-donor substituents, (*b*) steric interference due to certain other *ortho*-substituents, (*c*) steric interference due to the size of the alkyl group R.

The formation of hydrogen bonds by the amido-group, $-NH\cdot CO-$, has been the subject of previous parts of this series (*J.*, 1937, 1114; 1938, 375, 1034; 1939, 484; 1940, 332), and further indication of this tendency has been provided by *X*-ray investigation of acetamide (Senti and Harker, *J. Amer. Chem. Soc.*, 1940, **62**, 2008), urea (Wyckoff and Corey, *Z. Krist.*, 1934, **89**, 462), diketopiperazine (Corey, *J. Amer. Chem. Soc.*, 1938, **60**, 1598), and polypeptides

(Hughes and Moore, *ibid.*, 1942, **64**, 2236), and by the infra-red spectroscopic study of proteins (Buswell, Krebs, and Rodebush, *J. Physical Chem.*, 1940, **44**, 1126). It therefore seemed probable that esters of carbamic acid in which this grouping is present (I and II) would possess

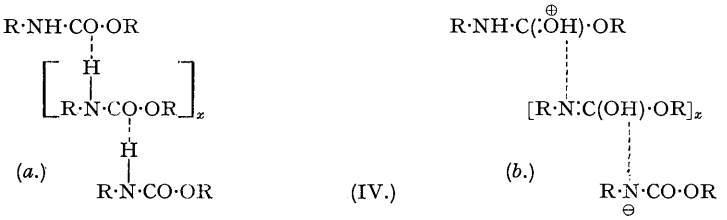
$NH_2 \cdot CO_2R$ (I.) $NHR \cdot CO_2R'$ (II.) $NRR' \cdot CO_2R''$ (III.)

a hydrogen-bond structure. Indication of hydrogen-bond association in these compounds is provided in their boiling points (see Table), those of the esters possessing one or more hydrogen

	B. p.		B. p.
$NH_2 \cdot CO_2Me$	177°	$NH_2 \cdot CO_2Et$	184°
$NHMe \cdot CO_2Me$	158	$NHMe \cdot CO_2Et$	170
$NHEt \cdot CO_2Me$	165	$NHEt \cdot CO_2Et$	175
$NMe_2 \cdot CO_2Me$	131	$NMe_2 \cdot CO_2Et$	147
$NEt_2 \cdot CO_2Me$	155	$NEt_2 \cdot CO_2Et$	169—172
		$NMe(OMe) \cdot CO_2Et$	155
		$NMe(OEt) \cdot CO_2Et$	167

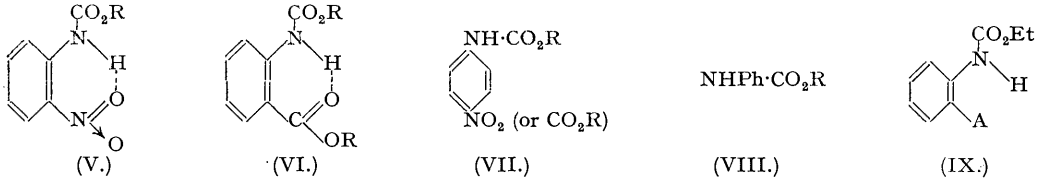
atoms (as in I and II) being higher than those of esters in which such atoms are completely replaced by simple alkyl or alkoxyl groups (III).

In the present investigation this prediction has been fully confirmed. The molecular condition of the esters of carbamic acid has been examined cryoscopically in benzene and in naphthalene solution over a range of concentration. As in previous parts of this series, molecular association is inferred from 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 indicating the absence of association. It is clear from the results (Fig. 1) that the esters fall sharply into two classes; those possessing at least one unsubstituted imino-hydrogen atom (as in I and II) are highly associated, whereas those in which both imino-hydrogen atoms have been replaced (as in II) are substantially unimolecular. This subdivision is in harmony with the tautomeric behaviour manifested by the former type but absent in the latter, and it seems clear that carbamates such as (I) and (II) owe their molecular association no less than their tautomerism to molecular union through hydrogen bonds (N–H–O), the imino-hydrogen atom of one molecule being shared with the carbonyl-oxygen atom of a second, as in the amides and sulphonamides (Chaplin and Hunter, *J.*, 1937, 1114). Such derivatives of carbamic acid therefore provide a further example of mesohydric tautomerism



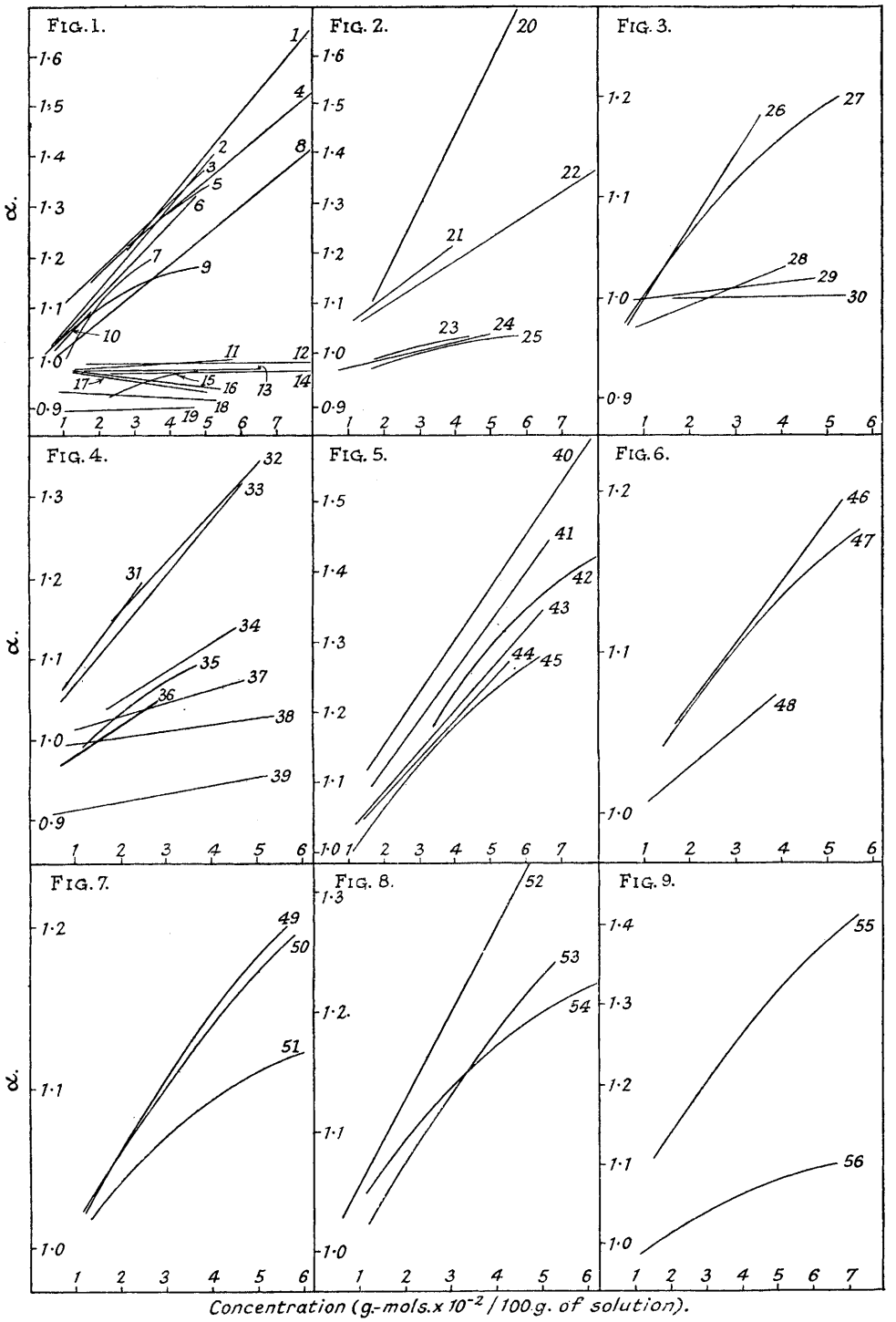
(Hunter, *J.*, 1945, 806). A chain polymer embodying these requirements and consisting of $x + 2$ molecules of the ester (II) is depicted in (IV), where (*a*) and (*b*) are unperturbed states of the resonance hybrid. Multi-membered cyclic polymers of the type found in acetamide (Senti and Harker, *loc. cit.*), involving no separation of charges, are equally probable.

That the imino-hydrogen atom of carbamic esters is responsible for their molecular association is confirmed not only by the fact that its replacement destroys association (Fig. 1), but also that its engagement in chelate ring-formation with suitable donor *ortho*-substituents (NO_2, CO_2R)



(V.) (VI.) (VII.) (VIII.) (IX.)

is similarly effective in suppressing molecular association. Thus, in ethyl *o*-nitro- (V) and ethyl *o*-carbomethoxy- (VI) phenylcarbamate, the preferential formation of *intramolecular* N–H–O



bonds so reduces the tendency of the imino-hydrogen atom to form intermolecular bonds that the compounds are virtually unimolecular (Figs. 2 and 3). In the corresponding *m*- and *p*-isomers (*e.g.*, VII), however, the relevant groups are too remote to achieve chelation, with the result that

the imino-hydrogen atoms are free to undertake intermolecular co-ordination, and the compounds are therefore associated (Figs. 2 and 3). In this connexion the remarkably high degree of association exhibited in benzene solution by ethyl *m*-nitrophenylcarbamate (Fig. 2, curve 20), since it is even higher than that of ethyl phenylcarbamate (Fig. 1, curve 6), is probably due in part to a heterogeneous association (Hunter and Marriott, *J.*, 1940, 166) between $-NO_2$ and $=NH$ groups in adjacent molecules. The low solubility in benzene of the *para*-substituted carbanilates (VII) necessitated measurement of their molecular weights in naphthalene solution, in which, owing to increased thermal agitation of the solute molecules consequent on the higher melting point of the solvent, lower factors of association are to be expected. This accounts for the relatively small slope of the curves for *iso*propyl *p*-nitrophenylcarbamate (Fig. 2, curve 21), ethyl *p*-nitrophenylcarbamate (Fig. 2, curve 22), and *methyl* and *ethyl* p-*carbethoxyphenylcarbamates* (Fig. 3, curves 26 and 27), which are nevertheless interpreted as indicating strong association.

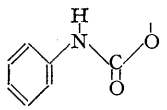
A remarkable consequence of the fixation of the carbethoxyamino-group in (VI) in a position co-planar with the benzene nucleus is the protection thus afforded to the 6-position even in face of reactive substituting agents such as bromine. Treatment of (VI) with bromine yielded only *ethyl* 4-*bromo*-2-*carbomethoxyphenylcarbamate* which, even with excess of bromine, failed to brominate further. Nor could a dibromo-compound corresponding to (VI) be obtained by the action of ethyl chloroformate on methyl 2 : 4-dibromoanthranilate, which failed to react under all conditions tried. Resistance to bromination has been recorded in similar circumstances for 3-nitroaceto-*p*-toluidide (Chaplin and Hunter, *J.*, 1938, 377).

A study of the carbanilates (VIII) and their derivatives has revealed that the capacity of the $-NH\cdot CO_2R$ group to cause molecular association is very sensitive to steric influences. For example, the high degree of association of ethyl phenylcarbamate (VIII; R = Et) is very markedly reduced by the substitution of groups in the *o*-position (*e.g.*, IX), as in ethyl *o*-tolyl-, ethyl 2 : 4-dimethylphenyl-, ethyl *o*-chloro- and -2 : 5-dichlorophenyl-, *ethyl* o-*bromophenyl*-, and *ethyl* o-*ethylphenyl*-carbamates (Fig. 4, curves 34—39). Such groups can scarcely be considered to engage the imino-hydrogen atom in chelate ring-formation, and it seems justifiable to assume that they play a mainly steric rôle. It would appear that the *o*-substituent A (IX), by virtue of its size, not only orientates the group $-NH\cdot CO_2R$ in such a way that the $-CO_2R$ group is remote from A, but that the latter, by its very bulk, discourages the approach of a second molecule sufficiently closely to the imino-hydrogen atom to engage it in intermolecular N–H–O bond-formation, thus substantially reducing the proportion of associated molecules. On the other hand, *m*- and *p*-isomers of (IX) (Fig. 4, curves 31—33), in which no such effects would be expected, show a degree of association which is much higher and comparable with that of ethyl phenylcarbamate itself. Ortho-effects of this kind have previously been noted in numerous other instances; *e.g.*, Hewitt and Winmill (*J.*, 1907, 441) reported a similar tendency in the degree of association of liquid phenols measured by the Ramsay–Shields method.

That hindrance of this kind is probably not the only factor controlling the degree of association in the above examples is indicated in Fig. 8, which compares ethyl phenylcarbamate with *methyl* and *ethyl* cyclo*hexylcarbamates*. The reduced association of the latter (curves 53 and 54) as compared with the former (curve 52) can clearly not be ascribed to steric causes, and is probably attributable to reduced acidity of the imino-hydrogen atom owing to the absence of a mesomeric effect in the latter. There are numerous other examples of the tendency to form hydrogen bonds being the stronger the more acidic the nature of the hydrogen atom concerned (see, *e.g.*, Hunter and Marriott, *J.*, 1941, 777).

Further effects attributable to steric causes are revealed by varying the group R in the carbanilates (VIII). Fig. 5 shows that the slope of the association–concentration curves of these esters in benzene solution undergoes progressive diminution with increasing size and complexity of the alkyl group (R); *i.e.*, the molecular association diminishes in the order R = Me > Et > *n*-Pr > *n*-Bu > *iso*-Pr > *iso*-Bu (Curves 40—45 respectively). Inspection of the structural formula of these compounds will show that, because of free rotation about the various single bonds, the molecule can assume a great number of different configurations, one being depicted in (X). It is evident that the larger the volume of the group R the greater will be its effect in hindering the approach of a second molecule towards the imino-hydrogen atom as a preliminary to hydrogen-bond formation. This explanation is in harmony with the above order, from which it is evident that the branching of the alkyl chain as well as its length plays an important part in the sheltering effect of the alkyl group towards the imino-hydrogen atom. The series of carbanilates shown in Fig. 5 could not be pursued beyond the *iso*butyl compound because of the limited solubility in benzene of the succeeding homologues; but a similar order

of steric effect was found in the butyl carbanilates by measurements in naphthalene solution, in which the compounds are more soluble owing to the higher melting point of the solvent. As



(X.) $CH_2Ph{\cdot}NH{\cdot}CO_2Et$ (XI.) $NHPh{\cdot}CH_2{\cdot}CO_2Et$ (XII.)

would be expected from the above steric hypothesis, *tert.*-butyl carbanilate (Fig. 6, curve 48) has a lower degree of association than the *iso*butyl isomer (Fig. 6, curve 47); ethyl carbanilate (Fig. 6, curve 46) was measured in naphthalene for comparison. It is interesting, though not unexpected, that phenyl carbanilate (Fig. 7, curve 49) is associated to about the same extent as ethyl carbanilate (Fig. 6, curve 46). These results are in close correspondence with those obtained from a study of the infra-red absorption spectra of the isomeric hexyl alcohols (Stanford and Gordy, *J. Amer. Chem. Soc.*, 1940, **62**, 1247), in which the degree of association is found to diminish with increasing branching of the carbon chain in the neighbourhood of the hydroxyl group.

The close connexion between hydrogen-bond association in the carbamic esters and their tautomeric character is strikingly illustrated by a comparison of ethyl benzylcarbamate (XI) with its isomer, ethyl phenylaminoacetate (XII). In the latter, the imino- and the carbonyl group are separated by a methylene-group, and not only is (XII) devoid of tautomeric character, but its molecular association (Fig. 9) is very markedly reduced in comparison with (XI), in spite of the presence in its molecule of the associating groups imino- and carbonyl. This predisposition on the part of tautomeric hydrogen to engage in hydrogen-bond formation has frequently been reported in previous parts of this series [*e.g.*, amides and imino-ethers (*J.*, 1937, 1114), pyrazoles and pyrazolines (*J.*, 1941, 3), thioacridone and thiodiphenylamine (*J.*, 1942, 640), cyanamides and aminoacetonitriles (*J.*, 1945, 618)], and provides a strong argument in favour of the theory of mesohydric tautomerism (*J.*, 1945, 806).

Experimental.

The following new compounds were prepared in the course of the investigation. *Methyl diethylcarbamate*, colourless liquid with peppermint odour, b. p. 154—155° (Found: N, 10·8. $C_6H_{13}O_2N$ requires N, 10·7%). *Ethyl dicyclohexylcarbamate*, colourless viscous liquid with peppermint odour, b. p. 304—306° (Found: N, 5·5. $C_{15}H_{27}O_2N$ requires N, 5·5%). *Methyl phenyl-n-butylcarbamate*, deep yellow oily liquid, b. p. 154°/21 mm. (Found: N, 6·6. $C_{12}H_{17}O_2N$ requires N, 6·7%). *Ethyl phenyl-n-butylcarbamate*, deep yellow oil, b. p. 156°/19 mm. (Found: N, 6·3. $C_{13}H_{19}O_2N$ requires N, 6·3%). *Ethyl 4-chloro-2-nitrophenylcarbamate*, obtained by prolonged boiling of 4-chloro-2-nitroaniline (2 mols.) and ethyl chloroformate (1 mol.) in carbon tetrachloride, formed yellow needles from alcohol, m. p. 99° (Found: N, 10·9. $C_9H_9O_4N_2Cl$ requires N, 11·5%). *Ethyl 3-nitro-p-tolylcarbamate*, prepared similarly from 3-nitro-*p*-toluidine, formed pale yellow needles from alcohol, m. p. 56—57° (Found: N, 12·9. $C_{10}H_{12}O_4N_2$ requires N, 12·5%). *Methyl p-carbethoxyphenylcarbamate*, white needles from aqueous alcohol, m. p. 151—152° (Found: N, 6·2. $C_{11}H_{13}O_4N$ requires N, 6·3%). *Ethyl p-carbethoxyphenylcarbamate*, white needles from aqueous alcohol, m. p. 129° (Found: N, 5·9. $C_{12}H_{15}O_4N$ requires N, 5·9%). *Ethyl 4-bromo-2-carbomethoxyphenylcarbamate*, white needles from alcohol, m. p. 94° (Found: N, 4·6; Br, 26·2. $C_{11}H_{12}O_4NBr$ requires N, 4·6; Br, 26·5%). *Ethyl o-ethylphenylcarbamate*, white platelets from aqueous

FIG. 1.

Concn.	*M.*	*a.*	Concn.	*M.*	*a.*
1. Ethyl β-naphthylcarbamate (215).			4. Ethyl methylcarbamate (103).		
2·90	262	1·22	2·86	126	1·22
4·40	290	1·35	4·80	137	1·33
6·16	322	1·50	6·73	149	1·45
7·93	354	1·65	10·38	173	1·68
			12·26	184	1·79
2. Ethyl *p*-methoxyphenylcarbamate (195).			5. Ethyl *p*-chlorophenylcarbamate (200).		
0·72	201	1·03	1·86	229	1·15
1·63	214	1·10	2·73	240	1·20
2·68	232	1·19	3·78	253	1·27
3·66	248	1·27	5·01	269	1·35
5·22	273	1·40			
3. Ethyl *p*-bromophenylcarbamate (244).			6. Ethyl phenylcarbamate (165).		
1·09	272	1·11	0·84	170	1·03
1·81	283	1·16	1·89	184	1·11
2·70	292	1·20	2·85	196	1·19
3·72	310	1·27	3·73	205	1·24
4·95	335	1·37	4·80	218	1·32

FIG. 1 (*continued*).

Concn.	*M.*	*a.*
7. Ethyl α-naphthylcarbamate (215).		
1·04	216	1·00
1·43	226	1·05
1·61	228	1·06
3·03	253	1·18
3·45	258	1·20
8. Ethyl ethylcarbamate (117).		
0·98	117	1·00
3·48	138	1·18
6·49	156	1·33
8·59	169	1·44
10·70	182	1·56
9. *iso*Propyl α-naphthylcarbamate (229).		
0·45	232	1·01
1·57	244	1·06
2·85	259	1·13
4·13	269	1·17
4·81	270	1·18
10. Ethyl *p*-ethoxyphenylcarbamate (209).		
0·85	213	1·02
1·22	216	1·04
1·72	227	1·09
11. Ethyl diphenylcarbamate (241).		
1·30	235	0·98
2·31	234	0·97
3·53	236	0·98
4·81	237	0·98
5·94	240	0·99
12. Ethyl diethylcarbamate (145).		
1·74	144	0·99
2·88	144	0·99
5·21	142	0·98
8·18	143	0·99
9·22	143	0·99
13. Ethyl dimethylcarbamate (117).		
1·66	115	0·98
2·83	113	0·96
5·16	113	0·96
5·91	114	0·97
6·55	115	0·98
13*a*. *Methyl diethylcarbamate* (131). (Coincident with Curve 13.)		
1·27	127	0·97
3·03	128	0·98
4·32	128	0·98
5·47	128	0·98
6·37	128	0·98

Concn.	*M.*	*a.*
20. Ethyl *m*-nitrophenylcarbamate (210).		
1·66	236	1·12
2·32	253	1·21
3·48	289	1·38
5·01	344	1·64
7·38	387	1·84
21. *iso*Propyl *p*-nitrophenylcarbamate (224).		
1·12	*242*	*1·08*
3·27	*267*	*1·19*
3·97	*273*	*1·22*
22. Ethyl *p*-nitrophenylcarbamate (210).		
1·58	*228*	*1·08*
3·80	*249*	*1·18*
6·00	*269*	*1·28*
8·22	*291*	*1·38*
14. *N*-Carbethoxypiperidine (157).		
2·29	154	0·98
3·41	153	0·98
4·64	152	0·97
6·11	153	0·98
8·27	152	0·97
15. Ethyl phenylmethylcarbamate (179).		
2·47	167	0·93
3·00	169	0·94
3·82	172	0·96
4·54	174	0·97
16. *Ethyl dicyclohexylcarbamate* (253).		
1·16	245	0·97
2·01	245	0·97
3·18	242	0·95
4·58	237	0·94
5·30	236	0·93
16*a*. *Methyl phenyl*-n-*butylcarbamate* (207). (Coincident with Curve 16.)		
1·05	201	0·97
2·21	199	0·96
3·05	196	0·95
3·67	196	0·95
4·68	195	0·94
17. *Ethyl phenyl*-n-*butylcarbamate* (221).		
1·21	215	0·97
2·14	213	0·96
3·35	208	0·94
4·21	207	0·94
4·99	205	0·93
18. *N*-Carbomethoxypiperidine (143).		
0·93	133	0·93
2·71	132	0·92
4·27	132	0·92
5·25	130	0·91
19. Ethyl phenylethylcarbamate (193).		
1·08	172	0·89
2·12	171	0·89
3·36	173	0·89
4·73	174	0·90

FIG. 2.

Concn.	*M.*	*a.*
23. Ethyl *o*-nitrophenylcarbamate (210).		
1·92	210	1·00
3·01	214	1·02
4·38	217	1·04
24. *Ethyl 4-chloro-2-nitrophenylcarbamate* (245).		
0·80	241	0·98
2·52	246	1·00
3·76	250	1·02
5·01	256	1·05
25. *Ethyl 3-nitro*-p-*tolylcarbamate* (224).		
1·82	220	0·98
2·49	224	1·00
4·03	230	1·03
5·15	232	1·04
5·85	233	1·04

FIG. 3.

Concn.	*M.*	α.
26. *Methyl* p-*carbethoxyphenylcarbamate* (223).		
0·78	*219*	*0·98*
2·67	*243*	*1·09*
3·45	*264*	*1·18*
27. *Ethyl* p-*carbethoxyphenylcarbamate* (237).		
0·69	*229*	*0·97*
1·87	*249*	*1·05*
3·28	*265*	*1·12*
4·26	*275*	*1·16*
5·26	*285*	*1·20*
28. *Ethyl* 4-*bromo*-2-*carbomethoxyphenylcarbamate* (302)		
0·92	294	0·97
1·73	295	0·98
2·56	302	1·00
3·37	309	1·02
4·10	312	1·03
29. Methyl *o*-carbomethoxyphenylcarbamate (209).		
0·90	212	1·01
1·70	207	0·99
2·66	208	1·00
3·51	208	1·00
4·77	215	1·03
30. Ethyl *o*-carbomethoxyphenylcarbamate (223).		
1·77	221	0·99
2·80	222	1·00
3·61	223	1·00
4·41	224	1·00
5·34	225	1·01

FIG. 4.

Concn.	*M.*	α.
31. Methyl *m*-bromophenylcarbamate (230).		
0·68	245	1·07
1·39	252	1·09
2·45	274	1·19
32. Ethyl *p*-chlorophenylcarbamate (see Curve 5).		
33. Ethyl *p*-tolylcarbamate (179).		
0·72	187	1·05
1·56	195	1·09
3·01	216	1·21
4·77	237	1·33
34. Ethyl 2 : 4-dimethylphenylcarbamate (193).		
1·82	201	1·04
2·50	206	1·07
3·35	211	1·09
4·50	219	1·14
35. Ethyl *o*-tolylcarbamate (179).		
1·12	177	0·99
1·59	181	1·01
2·08	186	1·04
3·04	191	1·07
3·69	195	1·09
36. *Ethyl* o-*ethylphenylcarbamate* (193).		
0·78	188	0·97
1·40	191	0·99
2·06	196	1·02
2·88	202	1·05
37. *Ethyl* 2 : 5-*dichlorophenylcarbamate* (234).		
0·98	238	1·02
1·87	239	1·02
2·69	241	1·03
3·62	245	1·05
4·78	254	1·08
38. *Ethyl* o-*bromophenylcarbamate* (244).		
0·95	241	0·99
2·60	246	1·01
3·25	248	1·02
4·25	248	1·02
5·42	251	1·03
39. Ethyl *o*-chlorophenylcarbamate (200.).		
0·52	181	0·91
2·00	183	0·92
3·79	188	0·94
4·66	190	0·95
5·20	190	0·95

FIG. 5.

Concn.	*M.*	α.
40. Methyl carbanilate (151).		
1·64	169	1·12
3·58	193	1·28
5·87	218	1·44
7·55	236	1·56
8·41	243	1·61
41. Ethyl carbanilate (165).		
1·77	181	1·10
4·35	218	1·29
6·43	235	1·43
42. *n*-Propyl carbanilate (179).		
3·39	211	1·18
5·65	237	1·32
6·93	247	1·38
8·17	255	1·43
43. *n*-Butyl carbanilate (193).		
1·28	200	1·04
3·93	235	1·21
4·87	242	1·25
5·61	251	1·30
6·43	259	1·34
44. *iso*Propyl carbanilate (179).		
1·48	187	1·05
3·31	207	1·16
3·89	213	1·19
5·11	223	1·25
5·55	227	1·27
45. *iso*Butyl carbanilate (193).		
1·06	194	1·00
2·92	218	1·13
3·91	226	1·17
4·80	234	1·21
6·28	247	1·28

FIG. 6.

Concn.	*M.*	α.
46. Ethyl carbanilate (165).		
1·80	*176*	*1·06*
4·11	*190*	*1·15*
5·23	*196*	*1·19*
47. *iso*Butyl carbanilate (193).		
1·47	*202*	*1·04*
2·96	*215*	*1·11*
3·83	*218*	*1·13*
4·79	*222*	*1·15*
5·69	*228*	*1·18*
48. *tert.*-Butyl carbanilate (193).		
1·07	*195*	*1·01*
2·68	*200*	*1·04*
3·96	*206*	*1·07*

FIG. 7.

Concn.	*M.*	α.
49. Phenyl carbanilate (213).		
1·24	*218*	*1·02*
2·37	*229*	*1·08*
4·15	*245*	*1·15*
5·66	*256*	*1·20*
50. *o*-Tolyl carbanilate (227).		
1·15	*231*	*1·02*
2·99	*249*	*1·10*
4·39	*261*	*1·15*
5·12	*265*	*1·17*
5·85	*272*	*1·19*
51. *cyclo*Hexyl carbanilate (219).		
1·39	*223*	*1·02*
3·24	*237*	*1·08*
4·70	*240*	*1·10*
5·98	*246*	*1·12*

FIG. 8.

Concn.	*M.*	α.
52. Ethyl phenylcarbamate (see Curve 6).		
53. *Methyl* cyclo*hexylcarbamate* (157).		
1·17	160	1·02
2·04	168	1·07
2·98	177	1·13
3·97	186	1·18
5·26	194	1·24
54. *Ethyl* cyclo*hexylcarbamate* (171).		
1·22	179	1·05
2·65	191	1·12
3·71	197	1·15
5·49	205	1·20
6·44	212	1·24

FIG. 9.

Concn.	*M.*	α.
55. Ethyl benzylcarbamate (179).		
1·59	198	1·11
2·84	213	1·19
4·79	230	1·29
5·93	241	1·35
7·19	253	1·41
56. Ethyl phenylaminoacetate (179).		
1·33	177	0·99
2·54	185	1·03
4·94	193	1·08
5·64	194	1·08
6·51	197	1·10
56*a*. Ethyl *o*-tolylaminoacetate (193). (Coincident with Curve 56.)		
1·70	195	1·01
2·62	199	1·03
3·81	203	1·05
5·39	208	1·08
7·40	213	1·10

alcohol, m. p. 43—45° (Found : N, 7·4. $C_{11}H_{15}O_2N$ requires N, 7·3%). *Ethyl* 2 : 5-*dichlorophenylcarbamate*, white needles from aqueous alcohol, m. p. 54° (Found : Cl, 30·3. $C_9H_9O_2NCl_2$ requires Cl, 30·3%). *Ethyl* o-*bromophenylcarbamate*, pale yellow liquid, b. p. 153°/16 mm. (Found : N, 5·6. $C_9H_{10}O_2NBr$ requires N, 5·7%). *Methyl* cyclo*hexylcarbamate*, white crystals from alcohol, m. p. 75° (Found : N, 8·9. $C_8H_{15}O_2N$ requires N, 8·9%). *Ethyl* cyclo*hexylcarbamate*, white crystals from alcohol, m. p. 55—56° (Found : N, 8·2. $C_9H_{17}O_2N$ requires N, 8·2%).

Revised melting points are recorded for the following : ethyl *p*-chlorophenylcarbamate, m. p. 70° (lit., 68°); ethyl *p*-methoxyphenylcarbamate, m. p. 67° (lit., 63—64°); ethyl 4-*m*-xylylcarbamate, m. p. 61° (lit., 58°); ethyl *o*-carbomethoxyphenylcarbamate, m. p. 67° (lit., 62°).

Molecular-weight Data.—Molecular weights were measured cryoscopically, the majority in benzene solution, but those recorded in italics in naphthalene solution. In the tables, concentrations are expressed as g.-mols. × 10^{-2}/100 g. of solution, the formula weights appearing in parenthesis; *M* is the apparent molecular weight deduced according to ideal-solution laws; the association factor (α) is calculated as the ratio of *M* to the formula weight.

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