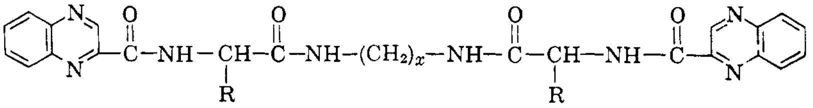
TABLE III

N,N′-{POLYMETHYLENEBIS[IMINOCARBONYL(SUBSTITUTED-METHYLENE)]}BIS-2-N″-QUINOXALINECARBOXAMIDES



R	x	Recrystallization solvents	M.p., °C.	Yield, %	Formula	Analyses Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
H	3	*p*-Dioxane	>200 dec.	37	$C_{25}H_{24}N_8O_4$	60.0	4.80	22.4	59.6	5.18	22.6
H	5	Dimethylformamide–water	>240 dec.	10	$C_{27}H_{28}N_8O_4$	61.4	5.30	21.2	61.4	5.12	21.0
H	6	Dimethylformamide–water	257 dec.	11	$C_{28}H_{30}N_8O_4$	62.0	5.54	20.6	62.1	5.80	20.2
H	10	Dimethylformamide–water	228–229	8	$C_{32}H_{38}N_8O_4$	64.2	6.35	18.7	64.0	6.52	18.8
$CH_2—C_6H_5$	5	Methanol	>170 dec.	12	$C_{41}H_{40}N_8O_4$	69.5	5.65	15.8	69.8	5.84	15.4

Anal. Calcd. for $C_{25}H_{33}N_5O_4$: C, 64.2; H, 7.07; N, 14.9. Found: C, 64.1; H, 7.36; N, 14.5.

General Synthesis of N,N′-[Polymethylenebis(iminocarbonylmethylene)]bisbenzoxycarboxamides (IX).—To a solution of one equivalent of the appropriate N-carbobenzoxyamino acid[16] and one equivalent of triethylamine in 250 ml. of toluene at −5° was added, with stirring, one equivalent of ethyl chlorocarbonate in 25 ml. of toluene. The resulting jell was held at −5° for 30 min., then one-half equivalent of the appropriate diamine in 25 ml. of toluene was added. Some evolution of carbon dioxide was noted. The mixture, which gradually thickened, was allowed to stand at room temperature overnight. The solvent was then distilled *in vacuo* and the residue was washed successively with water, dilute hydrochloric acid, water, dilute sodium carbonate, and water, followed by recrystallization from the appropriate solvent (see Table II).

General Synthesis of N,N′-{Polymethylenebis[iminocarbonyl(substituted-methylene)]}bis-2-N″-quinoxalinecarboxamides (IV).—A mixture of 0.05 mole of IX, 1 g. of 10% palladium on charcoal and 300 ml. of 95% ethanol containing 20 drops of glacial acetic acid was hydrogenated at 70° and 70 p.s.i. for 4 hr. The catalyst was removed by filtration from the clear reaction mixture and washed with methanol. The solvent from the combined washing and filtrate was distilled under reduced pressure. The thick oily residue was taken up in 50 ml. of 95% ethanol, and to this solution was added 0.2 mole of triethylamine. The resulting solution was added dropwise to a refluxing and stirred solution of 0.1 mole of II in 400 ml. of tetrahydrofuran. Almost immediately a precipitate appeared. The reflux period was extended for 15 min. and the reaction mixture was cooled and filtered. The crude solid product was washed successively with water, dilute hydrochloric acid, water, dilute sodium carbonate solution, water, and acetone, and purified by recrystallization (see Table III). These compounds are usually waxy in nature and hence extremely difficult to purify, which accounts for the relatively low over-all yields from IX.

Acknowledgment.—The authors wish to express their appreciation to Professor Roland K. Robins of Arizona State University for his suggestions and encouragement and to Mr. Hal P. Van Fossen and Mrs. Phyllis G. Lewis for their valuable assistance in performing the analytical measurements.

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(16) (a) M. Bergmann and L. Zervas, *Ber.*, **65**, 1192 (1932); (b) S. W. Fox, M. Fling, H. Wax, and C. W. Pettinga, *J. Am. Chem. Soc.*, **72**, 1862 (1950).

Reactions of the Perfluoroalkylnitriles. IV. Preparation and Characterization of Some N′-(Perfluoroacylimidoyl)perfluoroalkylamidines and Their Metal Chelates[1]

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Thermal condensation of perfluoroalkylamidines with the elimination of ammonia to yield 2,4,6-tris(perfluoroalkyl)-1,3,5-triazines was shown to proceed through an initial formation of the stable N′-(perfluoroacylimidoyl)perfluoroalkylimidines, $R_FC(:NH)N{=}C(NH_2)R_F$. Although originally isolated as their metal chelates, these compounds were easily synthesized from the reaction of perfluoroalkylamidines, $R_FC(:NH)NH_2$, with perfluoroalkylnitriles, and were prepared by this method for a detailed study of their properties. The N′-(perfluoroacylimidoyl)perfluoroalkylamidines appeared to exist predominantly in the "enolic" form; infrared and electronic spectra of these compounds and their metal chelates are discussed.

Thermal condensation of the perfluoroalkylamidines has been shown[2] to produce 2,4,6-tris(perfluoroalkyl)-1,3,5-triazines by the elimination of ammonia. This type of reaction was used subsequently to prepare a series of polymers containing *sym*-triazine rings connected by perfluoroalkyl chains that were stable at very high temperatures.[3]

Since the condensation reaction obviously involves three molecules of the perfluoroalkylamidine, the mechanism of the reaction is not readily apparent. This paper describes the study of the mechanism of the thermal condensation of the perfluoroalkylamidines and defines the nature of the first intermediate formed.

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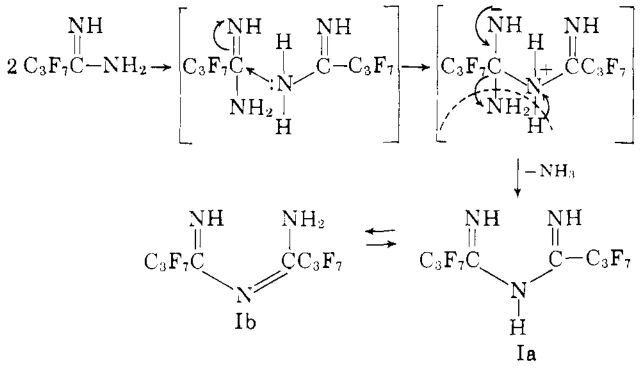
(1) This research was supported by the U. S. Air Force, Air Research and Development Command under contract AF 33(616)7971 monitored by Non-Metallic Materials Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Presented in part at the 140th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1961. Preceding paper in this series by H. C. Brown and D. Pilipovich, *J. Am. Chem. Soc.*, **82**, 4700 (1960). This paper represents a portion of the dissertation presented by Paul D. Schuman to the Graduate School of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) W. L. Reilly and H. C. Brown, *J. Org. Chem.*, **22**, 698 (1957).

(3) H. C. Brown, *J. Polymer Sci.*, **44**, 9 (1960).

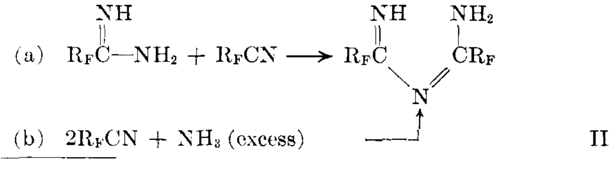
Attempts to study the kinetics of the initial stage of the thermal deammonation of perfluorobutyramidine (in pentachloroethane at 110°), with determination of the ammonia released and the triazine formed, showed that far less triazine was formed than would be required if each three moles of evolved ammonia indicated the formation of a mole of triazine. To account for these results, the presumption was made that the amidine was undergoing a condensation "dimerization" to give a stable intermediate. A possible mechanism was proposed in which the unshared pair of electrons of the amino nitrogen of one amidine molecule attacked the electron-deficient carbon of another amidine molecule; an unstable intermediate was formed which split out ammonia to become the stable N′-(perfluoroacylimidoyl)perfluoroalkylamidine, I, which may exist in either of two tautomeric forms, Ia and Ib.



Examination of the proposed structure Ib shows the possibility of chelate formation by coördinate covalent bonding of the metal ion to the imino nitrogen and covalent bonding to the amino nitrogen, with release of a proton from each molecule of I. Treatment of the reaction solution with Cu(II) ion readily formed the proposed chelate, thus supporting the structure shown.

A somewhat similar mechanism for the deammonation of trichloroacetamidine was discussed by Schaefer, *et al.*,[4] and a compound of structure similar to Ia was prepared by Dachlauer[5] by the reaction of trichloroacetonitrile with aqueous ammonia. Both Dachlauer and Schaefer found the trichloroacetamidine derivative to be unstable except at low temperatures.

Since knowledge of the physical and chemical properties of the N′-(perfluoroacylimidoyl)perfluoroalkylamidines would obviously be of importance in determining the complete mechanism of deammonation of amidines to triazines, this class of compounds was studied in detail. It was found that these compounds (shown in the generalized formula II) could be prepared in quantitative yields by the reaction of perfluoroalkylamidines with perfluoroalkylnitriles (a) or by the reaction of excess perfluoroalkylnitriles with anhydrous ammonia (b). Reaction (a) presents a method for preparing II with dissimilar R_F groups.



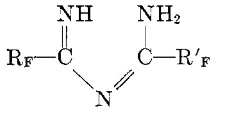
(a) $R_FC(=NH)-NH_2 + R_FCN \longrightarrow R_FC(=NH)-N=C(NH_2)R_F$

(b) $2R_FCN + NH_3$ (excess) $\longrightarrow$

II

Table I

N′ (Perfluoroacylimidoyl)perfluoroalkylamidines

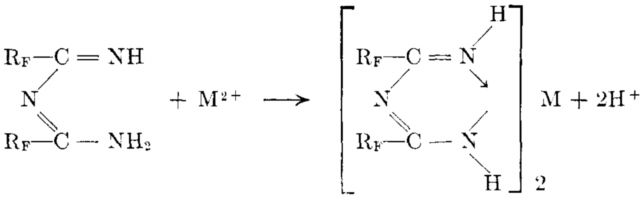


R	R′_F	B.p., °C.	d^{25}	n^{25}_D	Nitrogen, % Calcd.	Nitrogen, % Found
CF_3	CF_3	38–42 (m.p.)[a]	...	...	20.28	19.16
C_2F_5	C_2F_5	35.9–36.1 (6.8 mm.)	1.613	1.3438	13.67	13.41
C_3F_7	C_3F_7[b]	44.3–44.7 (1.5 mm.)	1.685	1.3386	10.31	10.50
CF_3	C_3F_7	50.0–50.8 (13.0 mm.)	1.652	1.3508	13.67	13.51
C_2F_5	C_3F_7	39.2–40.0 (3.8 mm.)	1.656	1.3398	11.76	11.38

[a] Decomposes at room temperature. [b] *Anal.* Calcd.: C, 23.58; F, 65.35. Found: C, 23.74; F, 65.11.

Properties of the N′-(perfluoroacylimidoyl)perfluoroalkylamidines prepared are shown in Table I. With the exception of the CF_3-substituted compound, all are liquids that may be distilled at low pressures without appreciable decomposition. N′-(Perfluorobutyrimidoyl)perfluorobutyramidine was easily hydrolyzed to N-(perfluorobutyryl)perfluorobutyramidine, $C_3F_7C(=O)NHC(=NH)C_3F_7$. The structure of this hydrolysis product was confirmed by its synthesis from the acylation of perfluorobutyramidine with perfluorobutyric anhydride and by its infrared spectra. N′-(Perfluoroacetimidoyl)perfluoroacetamidine was particularly susceptible to hydrolysis by atmospheric moisture.

The metal chelates, III, of the N′-(perfluoroacylimidoyl)perfluoroalkylamidines were prepared in essentially quantitative yields by reaction with solutions of the metal acetates. It was possible to follow the course of the chelation reaction by following the change in pH on addition of a standardized metal acetate solution; molecular weights of the ligands were confirmed by this method. The physical properties of the metal chelates are shown in Table II; these compounds were found to be soluble in a wide variety of polar organic solvents, less soluble in nonpolar solvents and quite insoluble in water. Since Cu(II) forms square, coplanar complexes, a search was made for possible geometric isomers in those chelates formed from N′-(perfluoroacylimidoyl)perfluoroalkylamidines with unlike R_F groups. No evidence was found that indicated the presence of such isomers.



III

The colors of the chelates were characteristic and are shown in Table II; as expected, copper and nickel, with their unfilled subshells, formed colored chelates while zinc and mercury, with completely filled subshells, formed colorless compounds.

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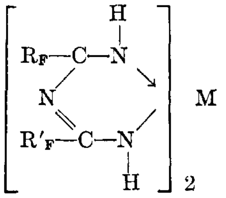
(4) F. C. Schaefer, I. Heckenbleikner, G. A. Peters, and V. P. Wystrach, *J. Am. Chem. Soc.*, **81**, 1466 (1959).

(5) K. Dachlauer, "Reactions of Trichloroacetonitrile," PB 58825, Office of the Publication Board, Department of Commerce, Washington, D. C.

TABLE II

N′-(PERFLUOROACYLIMIDOYL)PERFLUOROALKYLAMIDINE METAL CHELATES

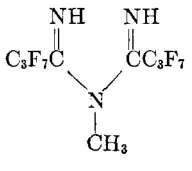


Ligand R_F	Ligand R'_F	Metal	M.p., °C.	Color[a]	Visible and ultraviolet absorption maxima[b] λ_{max}, mμ	log ε	λ_{max}, mμ	log ε	Analyses Metal,[c] % Calcd.	Metal,[c] % Found	Nitrogen,[d] % Calcd.	Nitrogen,[d] % Found
CF_3	CF_3	Cu	223 dec.	Maroon[e]	500 394	1.69 1.87	282	4.13	13.35	13.19	17.67	17.52
C_2F_5	C_2F_5	Cu	134–135	Maroon[f]	485 400	1.65 1.85	285	4.00	9.40	9.34	12.43	12.02
C_3F_7	C_3F_7	Cu	148.5–149.5	Maroon[f]	490 405	1.69 1.89	285	4.35	7.26	7.21	9.58	9.67
C_3F_7	C_3F_7	Zn	108.5–108.8	Colorless[f]	. . .	. .	290	4.18	7.41	7.31	9.58	9.39
C_3F_7	C_3F_7	Ni	152–153	Orange[f]	492	1.72	241 305	4.37 3.75	6.77	6.66	9.64	9.52
C_3F_7	C_3F_7	Hg	126–127	Colorless[f]	. . .	. .	289	3.83	19.93	20.39	8.30	8.53
CF_3	C_3F_7	Cu	114–115	Maroon[f]	500 396	1.65 1.84	284	4.15	9.40	8.97	12.43	12.10
C_2F_5	C_3F_7	Cu	102–103	Maroon[g]	490 405	1.67 1.87	284	4.06	8.18	8.08	10.82	10.56
C_7H_{15}	C_3F_7	Cu	135–136	Maroon	490 405	1.73 1.92	286	4.18	4.98	4.86	6.58	6.46

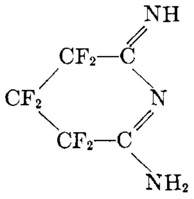
[a] As solution in crystallizing solvent. [b] Spectroscopic data determined on methanol solutions of the metal chelate using a Beckman DK-2 recording spectrophotometer. [c] Copper, nickel, and zinc determined electrolytically. Mercury determined as mercuric sulfide. [d] Analysis by Kjeldahl method. [e] Crystallized from benzene. [f] Crystallized from carbon tetrachloride. [g] Crystallized from hexane.

The absorption spectra in the ultraviolet region was of considerable interest in its providing evidence for the structure of the metal chelates and the N′-(perfluoroacylimidoyl)perfluoroalkylamidines. The initial assumption was made that the substituted amidines could exist in the tautomeric forms shown as Ia and Ib for N′-(perfluorobutyrimidoyl)perfluorobutyramidine. Determination of the ultraviolet absorption spectra of this compound showed a maximum at 262 mμ (log ϵ_{max} 3.93); a similar maximum does not appear in the spectra of perfluorobutyramidine (Table III) in which the imino group is not conjugated. One may reasonably assume, therefore, that conjugation contributes to the bathochromic shift of the maxima due to the chromophore $>$C=NH[6] and that the "enolic" form Ib is the most probable form.

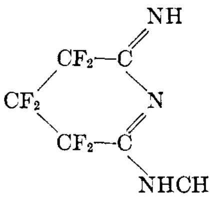
For further study of the effect of conjugation on the ultraviolet absorption of the N′-(perfluoroacylimidoyl)-perfluoroalkylamidines, several other fluorocarbon derivatives containing the imino group were prepared. N-(Perfluoroacylimidoyl)-N-methylperfluorobutyramidine IV, does not have a conjugated structure.[7] In the series of perfluoroglutarimidines,[3] V, VI and VII, the



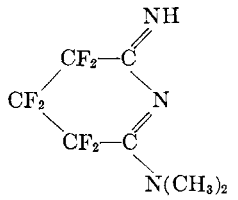
IV



V



VI



VII

first two might exist in the conjugated forms shown or in tautomeric, nonconjugated structures; the third imidine, VII, can have only the conjugated form.

Table III shows that IV has an inflection point in its ultraviolet absorption curve at 230 mμ; the bathochromic shift of absorption in this structure relative to perfluorobutyramidine must be due to the auxochromic effect $>N-CH_3$ group, with some slight $p-\pi$ conjugation from the nitrogen p electrons, which, however, is divided between two imino groups. This effect is also shown, somewhat more definitely, in the absorption by N,N-dimethylperfluorobutyramidine at 232 mμ.

N,N-Dimethylperfluoroglutarimidine, VII, must have the conjugated structure shown, and with the additional effect of the strong auxochrome, $-N(CH_3)_2$, shows absorption at 276 mμ. A shift of absorption to a higher frequency is shown by VI, in which the strength

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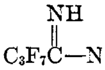
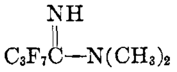
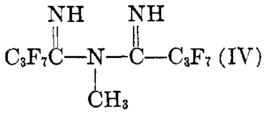
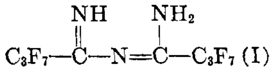
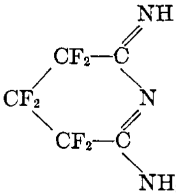
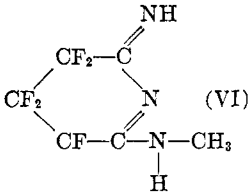
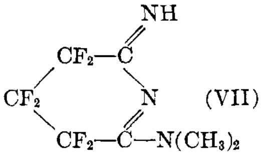
(6) The C=N bond (in aliphatic hydrocarbon derivatives) absorbs in the region of 190 mμ. Conjugation with C=C shifts this absorption about 30 mμ toward the red; it is probable that $\pi-\pi$ conjugation alone would not account for the absorption maxima found at 262 mμ for N′ (perfluorobutyrimidoyl)perfluorobutyramidine. Another influence is described below.

(7) N-(Perfluorobutyrimidoyl)-N-methylperfluorobutyramidine could be shown in other, isomeric structures. IV was chosen since formation of this compound by nucleophilic attack of the amino nitrogen of N-methylperfluorobutyramidine on the electron-deficient carbon of the C≡N group of perfluorobutyronitrile would certainly be preferred over attack by the more weakly basic imino nitrogen.

Table III

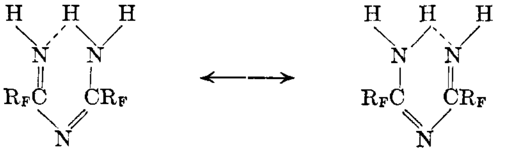
Ultraviolet Absorption Maxima of Perfluoroalkyl Compounds with Imino Groups[a]

Compound	λ_{max}, mμ	log ϵ_{max}
 $C_3F_7C(=NH)-NH_2$	<220	. . .
 $C_3F_7C(=NH)-N(CH_3)_2$	232	3.84
 $C_3F_7C(=NH)-N(CH_3)-C(=NH)-C_3F_7$ (IV)	230[b]	. . .
 $C_3F_7-C(=NH)-N=C(NH_2)-C_3F_7$ (I)	262	3.93
 (V)	254	4.22
 (VI)	259	4.23
 (VII)	276	4.28

[a] Spectroscopic data determined on methanol solutions of the compounds using a Beckman DK-2 recording spectrophotometer. [b] Inflection point.

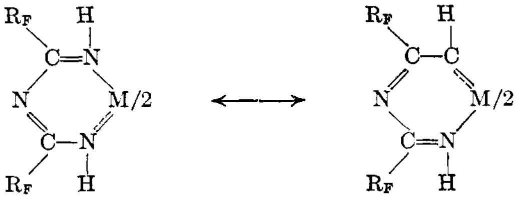
of the auxochrome has been decreased by removal of one methyl group, and the effect of $p-\pi$ conjugation diminished. However, the data indicates definitely that VI has the same conjugated structure as VII. The same reasoning may now be applied to the unsubstituted perfluoroglutarimidine, V, which absorbs at 254 mμ, and the conclusion reached that it also has the conjugated structure shown.

Structure V is obviously analogous to that of N′-(perfluorobutyrimidoyl)perfluorobutyramidine, Ib; the absorption for Ib, however, lies at a lower frequency than that for V. As an explanation for this difference, an additional structure is proposed for I (or II) in which intramolecular hydrogen bonding produces a six-membered ring. Resonance structures VIIIa and VIIIb (as


VIIIa VIIIb

the principal contributing forms) can be shown. Such forms require that the hydrogen be equidistant from the nitrogens, although not usually found in this position. The net result would be increased delocalization of the π electrons and consequent absorption at a lower frequency.

Ultraviolet absorption maxima of the metal chelates of the N′-(perfluoroacylimidoyl)perfluoroalkylamidines occurred at lower frequencies than those of the ligands, with the exception that the nickel chelate shows two maxima, one at 241 mμ and one at 305 mμ. For the chelates, the structures IXa and IXb may be considered, with the implication of partial multiple metal–nitrogen bonding in their benzenoid rings. Although


IXa IXb

some objection may be made to the increase in negative charge on the metal resulting from donation of electrons from the ligand, the stability of this type of structure may be favored by the strong electron-withdrawing properties of the perfluoroalkyl groups and the consequent electron deficiency of the entire ring. In any event, it is apparent from the shift of the absorption maxima that resonance in the ring becomes more important when the proton of the ligand is replaced by a metal which has orbitals available for double bond formation.

Assignments made in the infrared spectra of N′-(perfluorobutyrimidoyl)perfluorobutyramidine and its copper chelate are shown in Table IV with those of other fluorocarbon derivatives of similar structural features. In general, the absorption maxima obtained in the 2.5–6.6 μ region can be well correlated with the proposed structures.

N′-(Perfluorobutyrimidoyl)perfluorobutyramidine shows absorption characteristic of NH_2 symmetrical and asymmetrical stretching and a weak, broad band at 3.20 μ that can be assigned to an associated amino group. The copper chelate shows only weak N—H stretching.

In the region of C═N stretching, around 6 μ, assignment is difficult since N—H deformation absorption appears in the same region. To aid in differentiation between C═N stretching and N—H deformation, each of the compounds shown was synthesized with the hydrogen replaced by deuterium. The vibrational frequencies of N—D bonds should show a considerable shift[8] from those of N—H, while the C═N stretching should show little change. Unfortunately, a shift of this magnitude brings the absorption maxima of N—D (def.) into the region of the strong C—F stretching absorption where it cannot be seen. The net result on deuteration is a disappearance of an absorption maximum around 6 μ, thus identifying the maximum as N—H deformation. By this method a definite assignment was made for N—H deformation in N′-(perfluorobutyrimidoyl)perfluoroalkylamidine at 6.60 μ and in the corresponding copper chelate spectra at 6.54 μ. In confirmation of this method, the band at 6.15 μ (the so-

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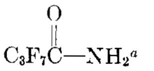
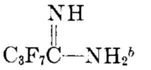
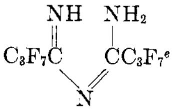
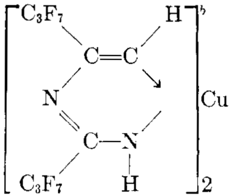
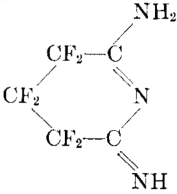
[8] In accordance with Hooke's law, $\nu = 1/2\,\pi\,(K/\mu)$, which relates the frequency, ν, K, the force constant of the bond, and μ, the reduced mass. For a change from N—H to N—D, the theoretical factor is 1.37.

TABLE IV

INFRARED ABSORPTION SPECTRA ASSIGNMENTS IN THE 2.5–6.6-μ REGION

Compound	N—H Assym. str.	N—H Sym. str.	N—H Assoc.	N—D Assym. str.	N—D Sym. str.	N—D Assoc.	C=N str. —C=NH	C=N str. —C≡N	C=N str. (deut.) —C=ND	C=N str. (deut.) —C≡N	N–H def.
 $C_3F_7C(=O)NH_2$[a]	2.82 (m)	3.03 (m)		4.00 (m)	4.30 (m)		(C = O 5.85 (s))		(C = O 6.02 (s))		6.15 (m)
 $C_3F_7C(=NH)NH_2$[b]	2.86 (m)	3.05 (m)		3.85 to 4.01[c]			5.71 (m)[d] 5.97 (s) 6.10 (m)[d]		5.75 (w)[d] 6.06 (s) 6.20 (w)[d]		
 $C_3F_7C(=NH)N=C(NH_2)C_3F_7$[e]	2.86 (m)	3.00 (w)	3.20 (w-b)	3.87 (m)	4.07 (m)	4.24 (w)	6.13 (s)	6.30 (s)	6.17 (s)	6.36 (s)	6.60 (w)
		2.93 (w)			4.00 (w)		6.25 (s)	6.45 (s)	6.29 (s)	6.47 (s)	6.54 (m)[d]
	2.89 (m)[d]	3.12 (m)		3.95 (m)		4.25 (m)	6.10 (m) 5.90 (m)[f]	6.30 (s)	6.10 (m)[d]	6.30 (s)	

[a] Nujol mull. [b] Kel-F Polymer Oil mull. [c] Triplet. [d] Shoulder. [e] Liquid state. [f] This maximum is not shown in the deuterated compound; N—H deformation at this frequency, however, is considered improbable, though possible.

called Amide II band) in perfluorobutyramide "disappeared" on deuteration.

No N—H deformation bands could be found in the spectra of perfluorobutyramidine. A somewhat puzzling absorption maximum appeared in the spectra of perfluoroglutarimidine at 5.90 μ which was not present in the deuterated analogue. Though this band may represent N—H deformation, it seems more probable that it is C—N stretching, and that its position was shifted slightly on deuteration, as some of the other C=N stretching frequencies are. Resolution of the spectra may not have been sufficient to show the band in the deuterated compound.

It is of interest also to note that the maxima at 6.13 and 6.30 μ in the N′-(perfluorobutyrimidoyl)perfluorobutyramidine spectra, which can now be definitely assigned to C=N stretching, are shifted to slightly longer wave lengths on formation of the chelate; this could be attributed to the increased effect of conjugation, with its lengthening of the original double bonds and consequent decrease in vibrational frequencies.

Experimental

Materials.—Perfluoroacetonitrile, perfluoropropionitrile, perfluorobutyronitrile, and perfluorocaprylnitrile were prepared by dehydration of the perfluoroalkylamides as described by Swarts[9] and by Gilman and Jones.[10] Perfluoroglutaronitrile was supplied by Hooker Chemical Corporation. Perfluorobutyramidine and perfluoroglutarimidine and their N-methyl derivatives were prepared by the method of Reilly and Brown.[2] Ammonia-d_3 was prepared by reaction of deuterium oxide with magnesium nitride.[11]

N′-(Perfluorobutyrimidoyl)perfluorobutyramidine.—Into an evacuated heavy-wall Pyrex glass ampoule of approximately 50-ml. capacity, previously constricted for sealing, were condensed perfluorobutyronitrile, 13.55 g. (0.0695 mole) and anhydrous ammonia, 0.391 g. (0.0230 mole), the ampoule being cooled by liquid nitrogen.

In order to moderate the exothermic reaction, the mixture was initially warmed to −78° and maintained at that temperature for 1 hr. Under these conditions the reaction tube contained a mixture of liquid and solid (perfluorobutyramidine). The ampoule was then warmed to 0° and held at this temperature for 23 hr. At the end of this period the reaction tube was opened to the vacuum system. On warming the tube to room temperature, 4.72 g. (0.0242 mole) of unchanged perfluorobutyronitrile was recovered. Remaining in the reaction tube was a quantitative yield (based on the unrecovered perfluorobutyronitrile) of colorless, liquid, N′-(perfluorobutyrimidoyl)perfluorobutyramidine, b.p. 44.3–44.7° (1.5 mm.); other physical properties and analyses are shown in Table I.

N′-(Perfluoropropionimidoyl)perfluoropropionamidine.—Perfluoropropionitrile, 10.08 g. (0.0695 mole) and anhydrous ammonia, 0.343 g. (0.0202 mole) were allowed to react in a heavy-wall glass ampoule, as described for the preparation of N′-(perfluorobutyrimidoyl)perfluorobutyramidine. The ampoule was opened after reaction and 0.131 g. (0.0282 mole) of unchanged perfluoropropionitrile recovered. Remaining in the tube was pure, colorless, liquid N′-(perfluoropropionimidoyl)perfluoropropionamidine. The purity was further substantiated by distillation through a glass-helices packed column; the entire product distilled at 35.9–36.1° (6.8 mm.).

N′-(Perfluoroacetimidoyl)perfluoroacetamidine.—Into an evacuated heavy-walled Pyrex glass ampoule of approximately 50-ml. capacity, cooled by liquid nitrogen, were condensed 6.79 g. (0.0715 mole) of perfluoroacetonitrile and 0.394 g. (0.0232 mole) of anhydrous ammonia. The reaction tube was warmed to −78° and held at this temperature for 30 min., then warmed to −24° and held for 1 hr. Under these conditions the reaction mixture was converted to a white solid. The reaction tube was then warmed to 0°, reopened to the vacuum system and 2.09 g. (0.0220 mole) of unchanged perfluoroacetonitrile recovered. Remaining in the reaction tube was 5.09 g. of a white, crystalline N′-(perfluoroacetimidoyl)perfluoroacetamidine, m.p. 38–42°. The additional nitrile consumed (0.295 g., 0.0031 mole) over the theoretical amount was shown in earlier experiments to be converted to 2,4,6-tris(perfluoromethyl)-1,3,5-triazine. When this reaction was carried out using smaller quantities of reactants, with better thermal control, quantitative yields were obtained.

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(9) F. Swarts, *Bull. classe sci. acad. roy. Belg.*, [5] **12**, 692 (1926).

(10) H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **65**, 1458 (1943).

(11) H. S. Taylor and J. C. Jungers, *ibid.*, **55**, 5057 (1933).

Some difficulty was encountered in storage and analysis of N′-(perfluoroacetimidoyl)perfluoroacetamidine since it was found to hydrolyze rapidly on exposure to the atmosphere; the hydrolysis product is presumed to be analogous to that of N′-(perfluorobutyrimidoyl)perfluorobutyamidine, which was shown to hydrolyze to N-(perfluorobutyryl)perfluorobutyramidine on exposure to atmospheric moisture. N′-(Perfluoroacetimidoyl)perfluoroacetamidine was also found to decompose slowly at room temperature, in the absence of moisture, to a liquid–solid mixture of undetermined composition.

N′-(Perfluoroacetimidoyl)perfluorobutyramidine.—Perfluorobutyramidine, 25.91 g. (0.1222 mole) was placed in a 250-ml. flask containing a Teflon-coated stirring bar. The flask was attached to a calibrated vacuum system and pumped free of air. Measured amounts of perfluoroacetonitrile were brought in contact with the solid perfluorobutyramidine at an average pressure of 400 mm. while the reaction mixture was maintained at 0°. After approximately 50% of the theoretical amount of nitrile had reacted, the reaction mixture was sufficiently fluid for stirring. Stirring was continued over a period of 8 hr.; during this time a pressure of perfluoroacetonitrile was maintained over the reaction mixture and 99% (11.48 g., 0.1208 mole) of the theoretical amount of nitrile reacted. Continued exposure of the reaction mixture to perfluoroacetonitrile resulted in no further reaction. The liquid product was distilled through a packed column at reduced pressure to yield pure N′-(perfluoroacetimidoyl)perfluorobutyramidine, b.p. 47.0–48.0 (7 mm.). This product decomposed slowly at room temperature in sealed tubes.

N′-(Perfluoropropionimidoyl)perfluorobutyramidine.—Perfluorobutyramidine, 10.92, (0.0505 mole) was placed in a heavy-wall Pyrex glass ampoule of approximately 50-ml. capacity. The ampoule was constricted for sealing and pumped free of air. Perfluoropropionitrile 9.70 g., (0.0669 mole) was condensed into the ampoule using liquid air as coolant. The ampoule was sealed and warmed to room temperature and held at this temperature for 48 hr. The ampoule was reopened to the vacuum system and unreacted perfluoropropionitrile, 3.87 g., (0.0267 mole) was recovered. Remaining in the reaction tube after removal of the excess nitrile was 16.7 g. of a clear liquid. Distillation of this product at reduced pressure gave a yield of 81% (based on the unrecovered perfluoropropionitrile) of N′-(perfluoropropionimidoyl)perfluorobutyramidine, b.p. 39.2–40.0 (3.8 mm.); this product was stored at room temperature under vacuum for extended periods with no decomposition.

N′-(Perfluorocaprylimidoyl)perfluorobutyramidine.—Perfluorobutyramidine, 3.24 g., (0.0104 mole) was dissolved in 25 ml. of methylene chloride in a 200-ml. flask equipped with a reflux condenser, a nitrogen sweep inlet tube and a dropping funnel. Perfluorocaprylonitrile, 6.62 g., (0.0160 mole) dissolved in 60 ml. of methylene chloride, was added with stirring over a period of 20 min. while the temperature of the reaction mixture was maintained at 30°. After complete addition of the nitrile, the reaction mixture was refluxed for 3 hr. The methylene chloride solvent was removed at reduced pressure to yield 8.33 g. of slightly viscous, cloudy liquid which presumably contained excess perfluorocaprylonitrile. N′-(Perfluorocaprylimidoyl)perfluorobutyramidine was isolated only as its Cu(II) chelate (Table II).

N-(Perfluorobutyrimidoyl)-N-methylperfluorobutyramidine.—Perfluorobutyronitrile, 13.22 g., (0.0678 mole) and methylamine, 0.701 g., (0.0226 mole) were sealed in a heavy-wall glass ampoule and allowed to react in a stepwise manner as described for the preparation of N′-(perfluorobutyrimidoyl)perfluorobutyramidine. N-Methylperfluorobutyramidine was formed initially at −78°; this reaction was followed by reaction of the excess nitrile with the N-methylperfluorobutyramidine at 0°. Unchanged perfluorobutyronitrile, 1.13 g., (0.0058 mole) was recovered; remaining in the reaction tube was a solid–liquid-mixture. The solids were separated by filtration and crystallized from hexane to give 2.55 g. (37%) of white, crystalline N-(perfluorobutyrimidoyl)-N-methylperfluorobutyramidine, m.p. 45.5–47.0°.

Anal. Calcd. for $C_9H_5F_{14}N_3$: C, 25.65; H, 1.19; N, 9.98. Found: C, 25.86; H, 1.33; N, 9.88.

N-(Perfluorobutyryl)perfluorobutyramidine.—Perfluorobutyric anhydride, 30.0 g., (0.0731 mole) was placed in a 100-ml. flask containing a Teflon-covered magnetic stirring bar. Perfluorobutyramidine, 4.0 g., (0.0188 mole) was added slowly with stirring at 30°. The reaction mixture was poured into water and formed two layers; this mixture was extracted with ether and the ether extract repeatedly washed with water. Evaporation of the ether solution at reduced pressure yielded 6.1 g. of N-(perfluorobutyryl)perfluorobutyramidine which was soluble in dilute, aqueous alkali and was precipitated from the basic solution on acidification. Recrystallization from tetrahydrofuran gave white, crystalline N-(perfluorobutyryl)perfluorobutyramidine, m.p. 224° dec.

Anal. Calcd. for $C_8H_3F_{14}N_2O$: C, 23.45; H, 0.49; N, 6.85. Found: C, 23.79; H, 0.43; N, 6.68.

The infrared spectra of N-(perfluorobutyryl)perfluorobutyramidine was identical with that of the hydrolysis product of N′-(perfluorobutyrimidoyl)perfluorobutyramidine and the hydrolysis product of its Cu(II) chelate.

N′-(Perfluorobutyrimidoyl)perfluorobutyramidine Copper(II) Chelate.—N′-(Perfluorobutyrimidoyl)perfluorobutyramidine, 5.43 g. (0.0133 mole) was dissolved in 100 ml. of carbon tetrachloride and mixed vigorously with an excess of aqueous 5% copper(II) acetate solution. A pink precipitate formed immediately. The precipitate was removed by filtration and the carbon tetrachloride layer separated and evaporated to dryness under reduced pressure. The combined solid product was washed with water and dried at 110° to yield 5.75 g. (98%) N′-(perfluorobutyrimidoyl)perfluorobutyramidine copper(II) chelate m.p. 148.5–149.5°.

The additional chelates shown in Table II were prepared in essentially the same manner and in comparable yields.