TABLE I
N-POLYFLUOROACYLAMINO DERIVATIVES

Compound	M.P., °C	Cryst. Solvent	Empirical Formula	Analyses Carbon Calc'd	Carbon Found	Hydrogen Calc'd	Hydrogen Found
2-Dfa[a] dibenzofuran	170–171	Heptane	$C_{14}H_9F_2NO_2$	64.4	64.2	3.44	3.50
2-Dfa fluorene	162–162.5	Heptane	$C_{15}H_{11}F_2NO$	69.5	69.4	4.25	4.36
2-Dfa-7-nitrofluorene	232–233	Xylene	$C_{15}H_{10}F_2N_2O_3$[b]				
2-Ppa[c] biphenyl	89–90	Hexane	$C_{15}H_{10}F_5NO$	57.1	57.0	3.17	3.31
2-Ppa fluorene	196–197	Benzene	$C_{16}H_{10}F_5NO$	58.7	58.7	3.05	3.00
2-Ppa dibenzofuran	184–185	Heptane	$C_{15}H_8F_5NO_2$	54.7	54.8	2.43	2.55
2-Ppa-9-fluorenone	240–241	Benzene	$C_{16}H_8F_5NO_2$	56.3	56.4	2.34	2.28
2-Ppa-7-acetylfluorene	215–216	Methanol	$C_{18}H_{12}F_5NO_2$	58.5	58.4	3.25	3.39
2-Ppa-7-nitrofluorene	220–221	Methanol	$C_{16}H_9F_5N_2O_3$	51.6	51.7	2.43	2.47
2-Pba[d] fluorene	190–191	Benzene	$C_{17}H_{10}F_7NO$	54.1	54.2	2.65	2.71
2-Pba biphenyl	93–94	Aq. Methanol	$C_{16}H_{10}F_7NO$	52.6	52.7	2.74	2.88
2-Pba dibenzofuran	178–179	Hexane	$C_{16}H_8F_7NO_2$	50.7	50.8	2.11	2.24
2-Pba naphthalene	122–123	Hexane	$C_{14}H_8F_7NO$	49.6	49.8	2.36	2.68
2-Pba-7-nitrofluorene	206	Xylene	$C_{17}H_9F_7N_2O_3$[e]	48.3	48.6	2.13	2.30

[a] Dfa = Difluoroacetylamino. [b] *Anal.* Calc'd: N, 9.21. Found: N, 9.11. [c] Ppa = Perfluoropropionylamino. [d] Pba = *n* Perfluorobutyrylamino. [e] *Anal.* Calc'd: N, 6.63. Found: N, 6.40.

Polyfluoroacyl Derivatives of Carcinogenic and Allied Amines[1]

EUGENE SAWICKI

Received December 5, 1955

In connection with a study of the physical properties of carcinogenic amines a number of difluoroacetyl, perfluoropropionyl, and perfluorobutyryl derivatives of carcinogenic and related amines have been synthesized, Table I. The study of the effect of fluoroacyl groups on the physiological properties of various types of biologically useful amines should prove of value.

EXPERIMENTAL[2]

Difluoroacetic anhydride. A mixture of 10.5 g. of difluoroacetic acid[3] and 7.8 g. of phosphorus pentoxide was refluxed for 2–3 hours, 2 g. of phosphorus pentoxide was added, and then the mixture was distilled. The yield of product, b.p. 125–127° was 80–90%.

Anal. Calc'd for $C_4H_2F_4O_3$: C, 27.6; H, 1.2. Found: C, 27.7; H, 1.4.

Perfluoropropionic anhydride. Perfluoropropionic acid[4] and phosphorus pentoxide were similarly allowed to react. The product was obtained in 75–85% yield, b.p. 70°. Lit. b.p. 69.8–70° at 735 mm.[5]

Perfluorobutyric anhydride. Perfluorobutyric acid[4] and phosphorus pentoxide treated as above gave the anhydride in 90–95% yield, b.p. 107–108°. Lit. b.p. 106–108°.[6]

General procedure for the preparation of the fluorinated acylamino derivatives. To a solution of 0.01 mole of the aromatic amine in 10 ml. of hot benzene was added 0.011 mole of the anhydride. For 7-acetyl- and 7-nitro-2-aminofluorene 10 ml. of hot xylene was used as the solvent. The mixture usually solidified in several minutes. Excess water was added and the benzene or xylene was steam-distilled. The crude product was crystallized from the appropriate solvent, Table I. Yields ranged from 80–95%.

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(1) This investigation was supported by research grant C-1066 from the National Cancer Institute, National Institutes of Health, Public Health Service.

(2) All melting points are uncorrected. Analyses were performed by the Peninsular ChemResearch, Inc., Gainesville, Florida.

(3) Difluoroacetic acid was obtained from the Peninsular ChemResearch, Inc.

(4) Perfluoropropionic acid and perfluorobutyric acid were obtained from the Minnesota Mining and Manufacturing Company, St. Paul 6, Minnesota.

(5) Husted and Ahlbrecht, *J. Am. Chem. Soc.*, **75**, 1605 (1953).

(6) Kirshenbaum, Streng, and Hauptschein, *J. Am. Chem. Soc.*, **75**, 3141 (1953).

Synthesis of Several Aromatic Isocyanides

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Received December 12, 1955

Although a number of aromatic isocyanides are known, there are no published syntheses of such compounds containing, in addition, functional groups which would increase their solubility in various body fluids. In view of the potential biological interest in such compounds, the synthesis of *p*-isocyanobenzoic acid and *p*-isocyanobenzenesulfonamide was attempted.

The problem was primarily one of isolation. It is necessary to remove the unstable product as soon as possible after acidification of the reaction mixture. This was accomplished with more success in the case of *p*-isocyanobenzoic acid. This product was sent to Professor L. Pauling whose interest in the type of compound described initiated this work.

EXPERIMENTAL

p-Isocyanobenzoic acid. To a refluxing mixture of *p*-aminobenzoic acid (27.4 g.), chloroform (13 ml.), and methanol (100 ml.), 20 alternate additions of powdered sodium hydroxide (3 g. each) and of a 60:40 mixture of

methanol-chloroform (5 ml. each) were made. Cooling was necessary to control the exothermic reaction after each addition. The additions took 2 hr. Heating under reflux was continued for 5 min. and the organic solvents were removed under reduced pressure. The solid residue was dissolved in water (1100 ml.), and ether (500 ml.) and 3% hydrochloric acid were added until the aqueous phase was acid to Congo Red, with vigorous stirring and ice-cooling. The ether extract was dried (sodium sulfate), the solvent was removed, and the residue was recrystallized from benzene-pentane; yield, 34%. The cream-colored solid darkened on heating but showed no definite m.p. below 300°. It was, however, pure and showed strong absorption in the infrared at 4.70 μ corresponding to the —N≡C group.

Anal. Calc'd for $C_8H_5NO_2$: C, 65.30; H, 3.43; N, 9.52; Neut. equiv., 147. Found: C, 65.08; H, 3.76; N, 9.26; Neut. equiv., 162.

p-Isocyanobenzenesulfonamide. To a refluxing mixture of *p*-aminobenzenesulfonamide (17.2 g.), sodium hydroxide (20 g.), and ether (50 ml.), was added dropwise with stirring a mixture of chloroform (28 ml.) and ethanol (5 ml.). The exothermic reaction maintained the mixture at the reflux. After the addition was complete (1 hr.), refluxing was continued for 15 min. The solvents were removed under reduced pressure and the solid residue was extracted with ethyl acetate in a Soxhlet extractor during 24 hr. After removal of the ethyl acetate, the cream-colored product was recrystallized from benzene, m.p. 235–237° (some softening at 120°); yield, 5%. Infrared absorption of —N≡C group at 4.71 μ.

Anal. Calc'd for $C_7H_6N_2O_2S$: C, 50.60; H, 3.64; N, 16.86; S, 19.27. Found: C, 50.94; H, 3.26; N, 16.42; S, 19.66.

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The Infrared Absorption Spectra of Nitroparaffins and Alkyl Nitrates[1,2]

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Received December 22, 1955

In the course of studying the chemistry of nitroparaffins and alkyl nitrates the infrared spectra of a large number of compounds have been determined. This paper summarizes and discusses our data.

Nitroparaffins. While four bands have been ascribed to the aliphatic nitro group a definitive assignment has yet to be made (*cf.* Table I).[3] The present investigation shows that the band in the 4.00–4.17 μ region is a very weak one, without value for diagnostic purposes.

TABLE I

INFRARED ABSORPTION BANDS PREVIOUSLY ASCRIBED TO THE ALIPHATIC NITRO GROUP

Wave Length (μ)				Ref.
4.00–4.17	6.29–6.49	7.25–7.58		*a*
	6.35–6.65	7.30–7.65		*b*
	6.4	7.4	11.75	*c*
	6.37–6.42	7.25–7.35	10.90–12.4	*d*
	6.38–6.45	7.24–7.38	10.90–11.97	*e*
	6.23–6.56	7.2–7.6		*f*

[a] Miller in Gilman's *Organic Chemistry*, Vol. III, p. 149, 1953, John Wiley and Sons, New York, N. Y. [b] Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950). [c] Shechter and Conrad, *J. Am. Chem. Soc.*, **76**, 2717 (1954). [d] Smith, Fan and Nielsen, *J. Chem. Phys.*, **18**, 707 (1950). [e] Haszeldine, *J. Chem. Soc.* 2526 (1953). [f] Randall, Fowler, Fuson, and Dangl, *Infrared Determination of Organic Structures*, p. 20, D. Van Nostrand Company, New York, N. Y., 1949.

While all previous workers have agreed that absorption characteristic of the aliphatic nitro group occurs in the 6.4 μ region there has been no way of telling just where to expect this band. It is now clear that primary and secondary nitro compounds absorb at 6.45 ± 0.01 μ and that tertiary nitroparaffins absorb at 6.51 ± 0.01 μ (Table II). In α-nitroesters this band is displaced to shorter wavelengths by *ca.* 0.05 μ. The striking regularity with which the band in the 6.4 μ region is found, plus the fact that it is unusually strong, renders it by far the most valuable infrared characteristic of aliphatic and alicyclic nitro compounds.[4]

Identification of the nitro band in the 7 μ region has been rather uncertain because of its proximity to a band associated with the methyl group. As a consequence previous assignments have been somewhat arbitrary. The data of Table II show that the band at 7.25 ± 0.02 μ is characteristic of primary nitro compounds for it is found regardless of whether or not a methyl group is present. Indeed, this is the only strong absorption band in the 7 to 7.5 μ region.

With secondary nitroparaffins band allocation in the 7 μ region is complicated by the occurrence of several bands in the 7 to 7.5 μ region. In the case of 2-nitropropane absorption maxima are found at 7.16, 7.30, and 7.37 μ. It is assumed that the peaks at 7.16 and 7.30 μ are due to the methyl groups of the isopropyl part of the molecule since such splitting is known to occur in isopropyl systems.[5] This leaves the band at 7.37 μ to be assigned to the nitro group. With 2-nitrobutane, and higher secondary open-chain nitro compounds, only two bands are observed in the 7.0 to 7.5 μ region. The one of longer wave length has arbitrarily been identified with the nitro group.[4] Although the methyl and nitro bands in this region are generally well separated, they are

(1) Paper XIV in the series "The Chemistry of Aliphatic and Alicyclic Nitro Compounds."

(2) This research was supported by the United States Air Force under Contract No. AF 18 (600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.

(3) See also, L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York, N. Y., 1954, pp. 250–251. Note the important paper by J. F. Brown which appeared after our work was completed [*J. Am. Chem. Soc.*, **77**, 6341 (1955)].

(4) This conclusion was previously reached by Smith, Fan, and Nielsen on the basis of much more limited evidence [*J. Chem. Phys.*, **18**, 707 (1950)].

(5) Foil Miller in Gilman's *Organic Chemistry*, Vol. III, p. 143, 1953, John Wiley and Sons, New York, N. Y.