TABLE II

MOLECULAR WEIGHT OF TRIFLUOROACETYL CYANIDE DIMER

T, °C.	33	33	33	33
Pressure, mm.	77	46	27.5	9
Mol. wt.	245	246	246	268

The authors wish to thank the Minnesota Mining & Manufacturing Company for their sponsorship of this work and for the supply of fluorocarbon carboxylic acids.

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The Preparation of Fluorocarbon Carboxylic Acid "Thiocyanates"[1]

BY R. H. PATTON AND J. H. SIMONS

RECEIVED SEPTEMBER 27, 1954

In a previous communication it was demonstrated that fluorocarbon carboxylic acid chlorides react with silver cyanide to yield fluorocarbon carboxylic acid cyanide dimers. It has now been determined that these acid chlorides also react readily with silver thiocyanate to yield fluorocarbon carboxylic acid thiocyanates.

These new thiocyanate derivatives are readily hydrolyzed by water and alcohols to yield, respectively, acids and esters plus thiocyanic acid.

A few of the physical properties of these new compounds are given in Table I.

TABLE I

Compound	B.p., °C.	d^{25}_4	Sulfur anal. Theory	Sulfur anal. Found	Mol. wt. of vapor Theory	Mol. wt. of vapor Found
$CF_3CO(SCN)$	72–74	1.369	20.64	20.82	155	154
CF_3CF_2CO-(SCN)	87	1.503	15.61	15.84	205	205
$CF_3(CF_2)_2CO$-(SCN)	106	1.644	12.55	13.13	255	256

Since all of these compounds were prepared by the same method, trifluoroacetyl thiocyanate will serve as an example.

Experimental

Trifluoroacetyl Thiocyanate.—Approximately 0.05 mole of trifluoroacetyl chloride was transferred to a heavy-wall Pyrex glass vial containing 13.3 g. (0.08 mole) of dry silver thiocyanate. The vial was sealed and placed in a water-bath for two days with the temperature maintained at 60–80°. The vial was then cooled in liquid air, opened and attached to a vacuum manifold system and the liquid contents transferred to another vial. The second vial was removed from the manifold system and the contents transferred to a small fractionating apparatus, avoiding as much as possible contact with atmospheric moisture. The product was then fractionated. The yield of colorless, mobile liquid, b.p. 72–74°, was 4.8 g. (0.03 mole).

Analysis.—The analysis of these compounds was performed by the usual Parr bomb gravimetric analysis for sulfur. The molecular weight of the vapor was calculated from vapor density measurements under the conditions of room temperature (approximately 30°) and the vapor pressure of the compound at that temperature.

Acknowledgment.—The authors are grateful to the Minnesota Mining and Mfg. Company for both the sponsorship of this work and the supply of fluorocarbon carboxylic acids.

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[1] The term "thiocyanate" is used in a general or generic sense as evidence of detailed structure is not available to distinguish between $CF_3\overset{\overset{\displaystyle O}{\|}}{C}SCN$ and $CF_3\overset{\overset{\displaystyle O}{\|}}{C}NCS$. Even for the organic analog of this substance the structure is not known with certainty, *e.g.*, A. E. Dixon and J. Taylor, *J. Chem. Soc.*, **93**, 696 (1908). Even if it were, it would be fallacious reasoning to assign a structure to the fluorocarbon derivatives by analogy.

Properties of Pure Normal Alkanes in the C_{17} to C_{36} Range

BY A. A. SCHAERER, C. J. BUSSO, A. E. SMITH AND L. B. SKINNER

RECEIVED OCTOBER 4, 1954

Although physical properties of some normal alkanes above n-$C_{20}H_{42}$ have been reported in the literature, the actual purity of these compounds is either not given or is estimated from melting curves. Melting curves are, of course, not reliable in view of the formation of solid solutions by adjacent members of this series. Also, there is a particular lack of data on the odd-number carbon normal alkanes of higher molecular weight.

In connection with some studies on properties of petroleum waxes we have prepared a series of pure normal alkanes, in the range n-C_{17} to n-C_{36}, which includes several of the odd-number carbon members. The pure compounds were obtained through a combination of various fractionation processes and the product purity established by high temperature mass spectrometric analysis.

In view of the fact that some of our data on the physical constants of these compounds vary somewhat from those reported by earlier investigators it was felt desirable to publish our results.

Experimental

Preparation of Pure Normal Alkanes.—The normal alkanes were isolated from a commercial crystalline type paraffin wax prepared from an East Texas lubricating oil distillate. The first step consisted of a urea extraction to eliminate the more highly branched isoparaffins and the cyclic compounds. The urea reactive portion was then distilled, at reduced pressure, into narrow fractions using a 90 cm. by 4 cm. i.d. vacuum jacketed column packed with protruded stainless steel packing. Each of the narrow boiling fractions was redistilled several times with heart cuts only being retained. Between each redistillation these heart cuts were contacted with an equal volume of 100% sulfuric acid, 30 minutes at 140°, followed by crystallization from toluene solution.

Purity at the completion of the first few cycles was estimated from automatic differential thermal analysis[1] data but products from subsequent cycles were submitted for high temperature mass spectrometric analysis. Purification cycles were repeated until a purity of 99% v.[2] or better was achieved.

Melting and transition temperatures are plotted in Fig. 1.

Heats of Fusion and Transition.—Heats of fusion and transition, shown in Table I and plotted in Fig. 2, were determined using an adiabatic calorimeter with electrical heating. The values obtained are accurate to within 2%.

Volume Contraction on Solidification and Transition.—Volume changes were determined with a conventional all glass dilatometer using mercury as the displacement liquid.

X-Ray Analysis.—These hydrocarbons were also examined at room temperature with X-rays using both single

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TABLE I

PHYSICAL CONSTANTS OF HIGH MOLECULAR WEIGHT NORMAL ALKANES

C No.	Mol. wt.	Purity, % v.[a]	M.p., °C.	Transition point, °C.	Density at 70°	n^{70}_D	Heat of fusion, ΔH_F, cal./mole	Heat of transition ΔH_T, cal./mole	Sum of heat of fusion and heat of transition $\Delta H_F + \Delta H_T$, cal./mole	% vol. contraction at Solidification	% vol. contraction at Transition
17	240.475	99.0	21.7	10.5	....	1.4170	...	..	...	..	..
18	254.502	99.9+	28.2	None	....	1.4191	14670	..	14670	..	..
19	268.529	99.5	32.0	22.8	....	1.4211	10950	3300	14250	10.5	2.5
20	282.556	99.9+	36.6	36.2	0.7550	1.4230	16700	[b]	16700	16.0	..
21	296.583	99.9+	40.2	32.5	.7583	1.4247	11400	3700	15100	10.0	2.5
22	310.610	99.7	44.0	43.0	.7631	1.4260	11700	6740	18440	10.0	6.2
23	324.637	99.6	47.5	40.5	.7641	1.4276	12900	5200	18100	9.4	4.2
24	338.664	99.9	50.6	48.1	.7657	1.4286	13120	7480	20600	9.5	5.2
25	352.691	99.8	53.5	47.0	.7693	1.4302	13800	6230	20030	9.6	4.8
26	366.718	99.8	56.3	53.3	.7704	1.4310	14220	7700	21920	9.8	6.0
27	380.745	99.0	58.8	47.1 53.0[c]	.7732	1.4321	14440	6920	21360	10.0	3.4
28	394.772	99.0	61.2	58.0	.7750	1.4330	15450	8470	23920	10.0	6.2
29	408.799	99.5	63.4	58.2	.7755	1.4340	15800	7100	22900	..	..
30	422.826	99.0	65.4	62.0	....	1.4348	...	..	...	..	..
36	506.988	99.0	75.9	72.1 73.8[d]	....	....	21230	9670	30900	..	..

[a] Purity determined by High Temperature Mass Spectrometer. [b] Transition temperature too close to melting point for ΔH_T to be determined. [c] Pure n-C_{27} has transitions at 47.1 and 53.0° with ΔH_T of 570 and 6350 cal./mole, respectively. [d] Pure n-C_{36} has transitions at 72.1 and 73.8° with ΔH_T of 2370 and 7300 cal./mole, respectively.

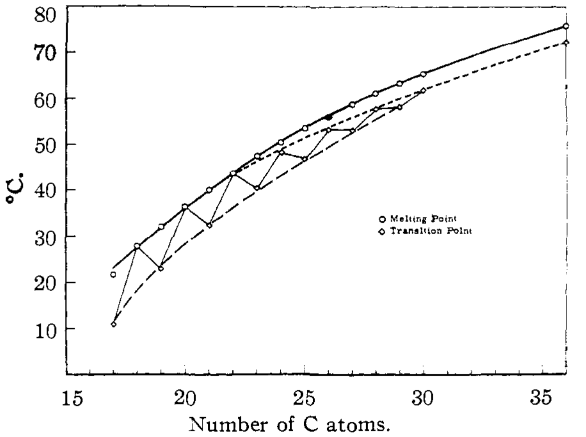

Fig. 1.—Melting and transition temperatures of high molecular weight normal alkanes.

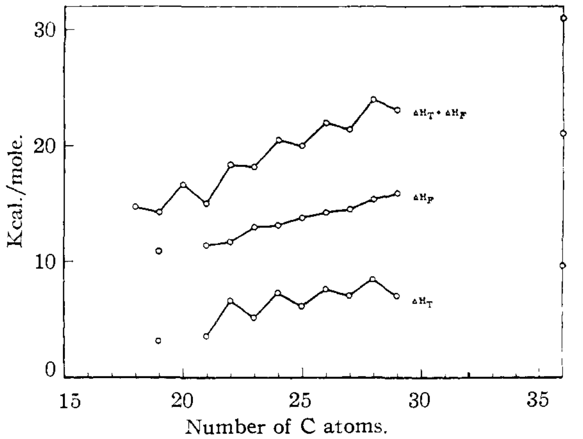

Fig. 2.—Heats of fusion and transition for high molecular weight normal alkanes.

crystal and powder methods. The single crystals were grown from toluene and xylene solutions.

Reflections were observed with n-$C_{23}H_{48}$ which are forbidden by the space group Pnam (D_{2h}^{16}) reported by Müller[3] for the low temperature form of n-alkanes containing an odd number of carbon atoms.

The detailed structures of the normal alkanes containing an odd number of carbon atoms in the range n-$C_{21}H_{40}$ to n-$C_{29}H_{60}$ were therefore determined. They are all orthorhombic, space group Pbcm (D_{2h}^{11}).

The lattice constants are listed in the table below (Table II).

TABLE II

LATTICE CONSTANTS OF NORMAL ALKANES (28°)

	a_0, Å.	b_0, Å.	c_0, Å.
n-$C_{21}H_{44}$	4.96(6) ± 0.01	7.47(0) ± 0.01	57.30 ± 0.08
n-$C_{23}H_{48}$	4.96(3) ± .01	7.46(4) ± .01	62.31 ± .10
n-$C_{25}H_{52}$	4.96(0) ± .01	7.45(5) ± .01	67.41 ± .08
n-$C_{27}H_{56}$	4.95(9) ± .01	7.45(0) ± .01	72.59 ± .08
n-$C_{29}H_{60}$	4.95(6) ± .01	7.44(3) ± .01	77.70 ± .18

Recent work by Müller and Lonsdale[4] and by Mazee[5] has shown that n-$C_{18}H_{38}$ and n-$C_{24}H_{50}$ are triclinic. Single crystal and powder data show that n-$C_{20}H_{42}$ and n-$C_{22}H_{44}$ are also triclinic. Both a triclinic and a monoclinic form were observed with n-hexacosane. Normal $C_{28}H_{58}$ and n-$C_{30}H_{62}$ are monoclinic, space group $P2_1/a$.

The addition of a few per cent. of neighboring homologs as impurities convert the triclinic and monoclinic forms, observed with the even number n-alkanes, into an orthorhombic form. The presence of impurities undoubtedly accounts for some of the earlier reports in the literature that even numbered n-alkanes in the range n-$C_{20}H_{42}$ to n-$C_{30}H_{62}$ are orthorhombic at room temperature.

Details of the X-ray structure investigation will be given elsewhere.

Acknowledgment.—We are indebted to Messrs. A. C. Hogge, G. P. Hinds, Jr., and M. J. O'Neal, Jr., of the Shell Oil Company, Houston Research

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Laboratories, for the high temperature mass spectrometric analyses.

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The Fluorides of Titanium: X-Ray Powder Data and Some Other Observations

BY KARL S. VORRES[1] AND FREDERIC B. DUTTON

RECEIVED MAY 28, 1954

Titanium trifluoride, prepared from the tetrachloride by reduction with aluminum in the presence of $AlCl_3$[2] and subsequent conversion with HF, was oxidized with chlorine. The resulting TiF_3Cl is a yellow powder which sublimes more readily than TiF_4, reacts with water to form a clear acid solution, and dissolves slightly in chloroform but neither in benzene nor in carbon tetrachloride. It hydrolyzes readily, and the air-stable product obtained by atmospheric hydrolysis and subsequent drying, both from it and from TiF_4, appears to be $TiOF_2$. The material so obtained and the oven-dried (100°) product of treating TiO_2 with 50% aqueous HF gave identical powder diffraction patterns. TiF_4 was prepared from the tetrachloride and anhydrous HF following Ruff[3] and others, and was purified by sublimation.

X-Ray powder diffraction data (Table I) were obtained for all the fluorides except TiF_3Cl, which was very finely divided and gave unsatisfactory patterns. Our data for TiF_4 disagree with the ASTM data[4]; these have previously been reported to be unreliable,[5] and comparison with the $TiOF_2$ pattern (see Table I) now shows that the original sample must have been predominantly $TiOF_2$. Except for $d = 2.18$ and $d = 1.20$, all the $TiOF_2$ lines of $d > 0.900$ appear in the ASTM data in proper position and sequence of intensity, and the three strongest $TiOF_2$ lines are the three strongest ASTM TiF_4 lines.

TABLE I

X-RAY POWDER DIFFRACTION DATA

TiF_3		TiF_4				$TiOF_2$	
		Obsd.		ASTM			
d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0
4.23	1	8.5	12	6.50	10	3.76	100^b
3.84	100	6.0	8	5.45	3	2.67	13
3.57^a	45	4.00	85	4.75	2	2.18	<1
3.11	10	3.79	1	4.35	2	1.89	31^b
2.71^a	25	3.68	100	3.80	100^b	1.69	32^b
2.31	6	3.09	35	3.56	2	1.54	7
2.08	100	2.68	10	3.40	2	1.34	13
1.92^a	45	2.35	2	3.22	20	1.26	11
1.80	85	2.22	4	2.68	12.5	1.20	1
1.72^a	45	2.01	10	2.35	3	..	<1
1.62	1	1.89	70	2.18	6	1.09	3
1.57	1	1.72	20	1.90	40^b	1.050	3
1.36^a	4	1.69	20	1.70	40^b	1.012	3
1.28	50	1.63	30	1.61	4	.949	<1
1.089	45	1.50	2	1.55	6	.921	4
1.042	20	1.39	17	1.485	1	.895	1
0.9033	6	1.34	17	1.345	12.5	...	<1
.8287	20	1.28	20	1.266	10	.850	4
.8074	15	1.25	2	1.098	2	.829	4
		1.04	1	1.054	2	...	<1
		1.00	1	1.015	2		
				0.921	2		

[a] Diffuse line. [b] Strongest lines.

The $TiOF_2$ lines may be given simple-cubic indices, and the report of a complete structural investigation is in press.[6]

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[1] Department of Chemistry, University of Southern California, Los Angeles, California.

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Metal–Amine Coördination Compounds. IV. Copper(I) Complexes

BY RONALD T. PFLAUM[1] AND WARREN W. BRANDT

RECEIVED DECEMBER 2, 1954

The copper(I) coördination compounds described are formed in the reaction of the copper(I) ion with 1,10-phenanthroline, 2,2′-bipyridine, 2,2′,-2″-terpyridine and 2,2′-biquinoline. Compounds of the first two chelating agents have received considerable attention in the past. Since the first observations on the color reaction,[2] many investigators have examined the absorption characteristics and the application of the complexes to the analytical determination of copper.[3–5] The formula of the 1,10-phenanthroline complex[4] and the stability of the 2,2′-bipyridine compound[6] have been determined, whereas the stability of the copper(I)–1,10-phenanthroline complex has not been evaluated.

The selectivity of 2,2′-biquinoline for the copper(I) ion accounts for the interest in it. This selectivity and the characteristics of the 2,2′-biquinoline complex in various non-aqueous solvents have been studied by several investigators.[4,7–9] Studies on substituted 1,10-phenanthroline reagents, which also exhibit selectivity for the copper(I) ion, have been carried out.[10–12] Most of the work has been done in immiscible alcoholic media with the emphasis toward application of the complexes to the determination of the copper.

No work has been reported on the copper(I)–2,2′,2″-terpyridine complex. An examination of

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[1] An abstract of a thesis submitted by Ronald T. Pflaum to the Graduate School of Purdue University, 1953, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. Present address, Dept. of Chem., State University of Iowa.

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