molecular weight arises from the presence of unreacted C_2F_6. There may be some other heavy gas present in small quantities, arising either from impurity or side-reaction.

The condensed fraction has, as nearly as may be judged, the composition, molecular weight, and vapor pressure (at −114°) to be expected from the proposed equation. The ratio of pressure of condensed gas to initial pressure is, however, low, so that it appears that not all of the original material is accounted for. In this connection it may be mentioned that small amounts of a gray-white solid product were deposited in the reaction system outside the furnace. A similar phenomenon was recorded by Swarts.[5] In our case this effect was more noticeable in some preliminary runs with slightly contaminated gas. During the rest of the runs the deposition was much less noticeable, but it apparently continued to some extent. Whether it was sufficient to account for the missing material is difficult to decide.

In the introduction it was indicated that a comparison with the measured decomposition of ethane might be significant. Schumacher's[10] summary of the studies of ethane indicate that homogeneous decomposition becomes appreciable at around 850°K. The fact that homogeneous decomposition of the hexafluoroethane is inappreciable nearly 250° higher indicates a degree of stability out of the class of the hydrocarbons.

Summary

On the basis of measurements in the range, 800–842°C., the thermal decomposition of hexafluoroethane in quartz has been demonstrated to be a complex heterogeneous reaction. Minimum temperature for reaction is about 600°, but it seems highly probable that homogeneous decomposition does not occur even at 842°. This places hexafluoroethane among the most stable of known organic compounds. In a quartz vessel the predominant reaction seems to be

$$C_2F_6 + 3/2SiO_2 \longrightarrow CO + CO_2 + 3/2SiF_4$$

with, however, some loss of material, which possibly is contained in a gray-white solid which distills out of the reaction flask.

CHAPEL HILL, NORTH CAROLINA
RECEIVED AUGUST 19, 1946

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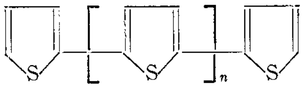
[10] Schumacher, "Chemische Gasreaktionen," Verlag Theodor Steinkopf, Dresden, 1938, p. 154.

[CONTRIBUTION NO. 1079 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Chromatographic and Spectral Characteristics of Some Polythienyls

BY J. W. SEASE[1] AND L. ZECHMEISTER

During an investigation of certain plant materials we became interested in some representatives of the α-polythienyl series, which is characterized by the following formula



While 2,2′-bithienyl (n = 0) has been known for some time,[1a] the compounds with n = 1 to 4 have been prepared only recently by Steinkopf and his collaborators.[2] They found that a mixture of several members of this series is formed by the interaction of 2-iodothiophene and copper bronze, and that the mixture can be separated by distillation and crystallization procedures. We wish to report that such a resolution can be advantageously carried out by chromatographing on alumina from petroleum ether or carbon bisulfide solution. The adsorption affinity decreases markedly with n, so that terthienyl, quaterthienyl, and quinquethienyl (n = 1 to 3) form well-separated zones whose migration can best be followed during development by their fluorescence in ultraviolet light. Bithienyl is rapidly washed into the filtrate. Furthermore, the Tswett column allows a homogeneity test by which traces of higher or lower members of the series may be easily detected in a given sample.

So far as we know the spectral curves of the polythienyls have not yet been reported. As expected, an increase of the number of thienyl residues in the molecule shifts the position of the main maximum toward longer wave lengths (Figs. 1–2; Table I). In hexane solution a secondary peak, whose position is independent (within 5

TABLE I

MOLECULAR EXTINCTION COEFFICIENTS (MAXIMA) FOR SOME α-POLYTHIENYLS

	In hexane		In benzene	
	mμ	$E^{\text{mol.}}_{\text{1 cm.}} \times 10^{-4}$	mμ	$E^{\text{mol.}}_{\text{1 cm.}} \times 10^{-4}$
Thiophene	231	0.56	...	..
Bithienyl	301	1.23	303	1.21
Terthienyl	350	2.31	355	2.19
Quaterthienyl	385	3.45	391	3.20
Quinquethienyl	...	..	418	3.81
1-Methyl-terthienyl	355	2.41	...	..
1,8-Dimethyl-terthienyl	359	2.61	...	..

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[1] Present address: Wesleyan University, Middletown, Conn.

[1a] *Cf.* the monograph, W. Steinkopf, "Die Chemie des Thiophens," Th. Steinkopff, Dresden, 1941.

[2] W. Steinkopf, R. Leitsmann and K. H. Hofmann, *Ann.*, **546**, 180 (1941).

mμ) of the number of the thienyl residues, can also be observed.

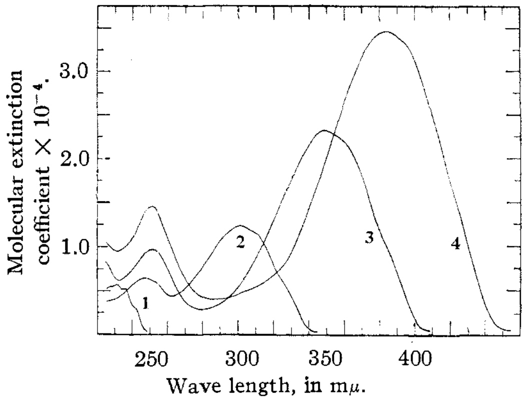

Fig. 1.—Molecular extinction curves of some α-polythienyls in hexane. The figures next to the curves denote the number of thiophene rings in the molecule.

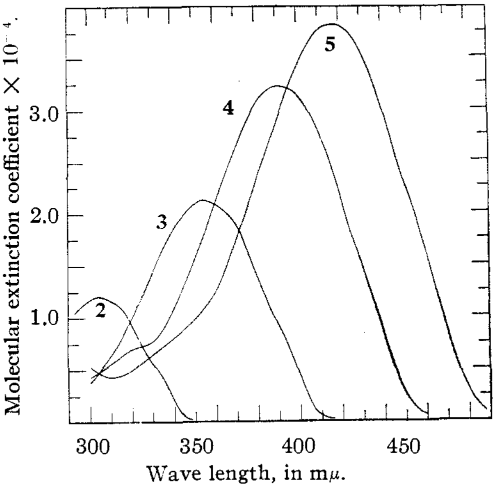

Fig. 2.—Molecular extinction curves of some α-polythienyls in benzene. The figures next to the curves denote the number of thiophene rings in the molecule.

Analogous experiments with 1,8-dimethyl-α-terthienyl, 1-methyl-α-terthienyl, and α-terthienyl showed that these compounds can also be separated on alumina columns since the adsorption affinities decrease from the dimethylated to the methyl-free compound. The introduction of each methyl group shifts the position of the main extinction maximum toward longer wave lengths by 4 to 5 mμ in hexane (Fig. 3).

Acknowledgment.—We are indebted for microestimations to Professor A. J. Haagen-Smit, Dr. G. Oppenheimer, and Mr. G. Swinehart.

Experimental

Materials and Methods.—The adsorbent used was alumina (Alorco, Grade F, 80 mesh, reground to 200 mesh), mixed with 10% Celite 535 as a filter aid. In order to standardize this adsorbent, which had stood in our Laboratory for some time, the following procedure was adopted[3]: Maximally activated material obtained by ignition was weakened by adding 0.7% water and shaking mechanically for two hours, after which the alumina was kept in a closed bottle for at least an additional twelve hours with occasional shaking. Chromatograms were observed either with a "Purple X" (General Electric Co.) or a "Wonderlite" (Wonderlite Co., West Orange, N. J.) incandescent ultraviolet lamp. The extinction curves were taken with a Beckman Spectrophotometer[4] and represent averages of independent determinations. The melting points, which are all corrected, were determined in an electrically heated Berl block. The substance (sealed under nitrogen) was introduced 25° below the melting point and the heating rate was 2° per minute.

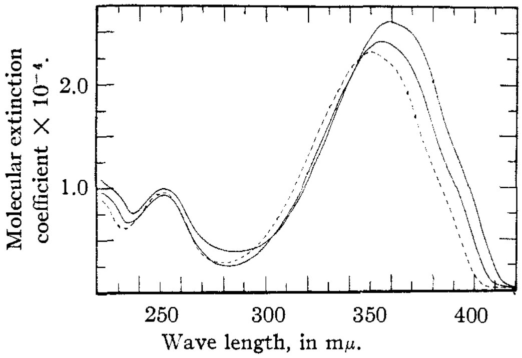

Fig. 3.—Molecular extinction curves of 1,8-dimethyl-α-terthienyl (top), 1-methyl-α-terthienyl (middle), and α-terthienyl (bottom; dashed line) in hexane.

Terthienyl, Quaterthienyl and Quinquethienyl.—A mixture of 28.8 g. of 2-iodothiophene and 18 g. of copper bronze was heated in an oil-bath at 200–210° for fifteen minutes. The product was extracted with 5 × 60 ml. of cold carbon disulfide.[2] After filtration and evaporation, as much of the residue as possible was dissolved in 10 × 12.5 ml. of petroleum ether (b. p. 60–70°) ("Fraction A," containing mainly bithienyl and terthienyl) and the remainder was taken up in 75 ml. of carbon disulfide ("Fraction B," mainly quaterthienyl and higher members).

Fraction A.—The solution was divided between two columns (21 × 7 cm.) and was developed with petroleum ether containing 3% acetone (the figures on the left denote the width of the zones, in mm.; fl. = fluorescence or fluorescent).

25 several brownish zones, no fl.
20 faint yellow, bluish fl.: unknown
10 colorless, non-fl. interzone
15 faint yellow, bluish fl.: unknown
35 interzone
25 faint yellow, bluish-green fl.: quaterthienyl
40 interzone
2 yellow, bluish fl.: terthienyl
40 empty bottom zone
Filtrate: colorless, no fl.: bithienyl

The quaterthienyl zone was eluted with methanol containing a little carbon disulfide. The evaporation residue was crystallized by dissolving in 5 ml. of carbon disulfide, adding one volume of petroleum ether and cooling slowly to 0°; the yield was 21 mg., m. p. 215–216°.

The ether eluate of the terthienyl zone was evaporated and the residue was crystallized from 40 ml. of hot methanol. After washing with cold methanol, 0.80 g. of platelets, m. p. 94–95.5°, was obtained. The mother liquor yielded an additional 0.17 g.

The chromatographic filtrate was concentrated at 50° to 5 ml. Upon dilution with methanol to 12 ml. and cooling, 2.45 g. of bithienyl crystallized, m. p. 32–33.5°

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[3] P. B. Müller, *Helv. Chim. Acta*, **26**, 1945 (1943); **27**, 404 (1944).

[4] H. H. Cary and A. O. Beckman, *J. Optical Soc. Am.*, **31**, 682 (1941).

(oil-bath). From the mother liquor a further 0.45 g. was obtained.

Fraction B.—The carbon disulfide solution was developed with benzene on a 22.5 × 7 cm. column.

40 several brownish zones
90 yellow, greenish-yellow fl.: quinquethienyl
10 interzone
40 yellow-green, bluish-green fl.: quaterthienyl
45 empty bottom zone

The **quinquethienyl** and **quaterthienyl** zones were eluted and crystallized as described for the latter under "Fraction A," using, however, 4 ml. and 8.5 ml. of carbon bisulfide, respectively. The yields were 22 mg. of quinquethienyl (m. p. 256–257°) and 137 mg. of quaterthienyl (m. p. 212–214°). Analytical samples of both compounds were recrystallized from hot ligroin (b. p. 86–100°).

Methyl-terthienyl.—A mixture of 5-iodo-5′-methyl-2,2′-bithienyl and 2-iodothiophene (1.5 g. each) was heated with 2.25 g. of copper bronze at 200° for four hours.[2] Extraction with 10 × 20 ml. of cold carbon disulfide and evaporation gave a residue which was extracted with 10 × 15 ml. of cold petroleum ether ("Fraction C," mainly terthienyl and methyl-terthienyl), and then with 125 ml. of cold carbon bisulfide ("Fraction D," mainly dimethyl-terthienyl).

Fraction C was developed on a 22 × 5.3 cm. column with petroleum ether containing 2% acetone.

20 yellow, orange fl.: unknown
50 faint yellow, bluish-green fl.: unknown
60 yellow, bluish-green fl.: dimethyl-quaterthienyl
40 interzone

$$\left.\begin{array}{l}\text{15 colorless, blue fl.}\\ \text{3 yellow, no fl.}\end{array}\right\}\text{methyl-terthienyl + terthienyl}$$

30 empty bottom zone

The dimethyl-**quaterthienyl** was eluted with methanol plus a little carbon bisulfide, evaporated and the residue dissolved in 100 ml. of benzene in which 23 mg. of dimethyl-quaterthienyl was found photometrically.

In order to separate terthienyl from its monomethyl derivative, the combined 15 mm. and 3 mm. zones were eluted with methanol, evaporated, taken up with 50 ml. of petroleum ether, and developed on a 28 × 7 cm. column with benzene plus petroleum ether (1:10).

180 colorless, no fl.
90 faint yellow, heterogeneous, bluish fl.: methyl-terthienyl + terthienyl
10 empty bottom zone

The two constituents of the fluorescing section overlapped. The lower third, which contained all of the terthienyl and some methyl compound was eluted, transferred to 75 ml. of petroleum ether and rechromatographed to obtain full separation.

120 colorless, no fl.
35 colorless, bluish fl.: methyl-terthienyl
10 interzone
20 colorless, bluish fl.: terthienyl
15 empty bottom zone

The **methyl-terthienyl** fraction was eluted with methanol and combined with the eluate of the upper two-thirds of the 90 mm. zone from the former chromatogram. Crystallization from 12 ml. of methanol yielded 153 mg.; m. p. 93–94.5°. An additional 34 mg. was obtained from the mother liquor. The terthienyl was estimated photometrically (40 mg.).

Fraction D.—The carbon disulfide solution was developed with benzene on a 23 × 5 cm. column.

12 dark brown
25 yellow, yellow fl.: unknown
10 interzone
110 greenish-yellow, bluish-green fl.: dimethyl-quaterthienyl
15 interzone
30 colorless, bluish fl.: methyl-terthienyl + terthienyl
30 empty bottom zone

The **dimethyl-quaterthienyl** was eluted, evaporated and crystallized from 13 ml. of hot ligroin (b. p. 86–100°); the yield was 70 mg., m. p. 172–173.5°.

The methyl-terthienyl plus terthienyl mixture was resolved on a 21 × 5 cm. column by developing with benzene plus petroleum ether (1:10).

140 colorless, no fl.
40 colorless, bluish fl.: methyl-terthienyl
5 interzone
10 colorless, bluish fl.: terthienyl
10 empty bottom zone

The **methyl-terthienyl** and **terthienyl** eluates were combined with the corresponding ones of Fraction C before crystallization, and the yields given there include this material, which amounted to less then one-seventh of the total.

Dimethyl-terthienyl.—A mixture of 1 g. of 5-iodo-5′-methyl-2,2′-bithienyl, 1 g. of 2-iodo-5-methylthiophene, and 2 g. of copper bronze was heated at 200° for four hours. The material was then extracted with 8 × 20 ml. of carbon bisulfide.[2] After evaporation, the residue was extracted with 10 × 20 ml. of petroleum ether ("Fraction E," mainly dimethyl-terthienyl), and then with 80 ml. of carbon disulfide ("Fraction F," mainly dimethyl-quaterthienyl).

Fraction E was developed (21 × 5 cm. column) with petroleum ether containing 1% and later 3% acetone.

50 brown, orange, and yellow; orange and yellow fl.: unknown
30 faint yellow, blue fl.: unknown
40 interzone
35 yellow, blue-green fl.: dimethyl-quaterthienyl
6 interzone
2 yellow, bluish fl.: unknown
10 interzone
2 yellow, bluish fl.: dimethyl-terthienyl
35 empty bottom zone

The dimethyl-**terthienyl** was eluted with methanol, evaporated and crystallized from 12 ml. of methanol; the yield was 113 mg., m. p. 98–99°. An additional 88 mg. was obtained from the concentrated mother liquor at 0°. The **dimethyl-quaterthienyl** was eluted with methanol, evaporated and estimated photometrically in benzene (27 mg.).

Fraction F.—The carbon disulfide solution was developed with benzene on a 21 × 5.3 cm. column.

40 brown and orange zones, yellow fl. in lower part: unknown
20 faint yellow, no fl.
25 yellow, greenish-yellow fl.: unknown
15 interzone
35 greenish-yellow, bluish-green fl.: dimethyl-quaterthienyl
75 empty bottom zone

The **dimethyl-quaterthienyl**, after elution and evaporation, was crystallized from 12 ml. of ligroin; the yield was 39 mg.

1,8-Dibromo-terthienyl.—To 165 mg. of terthienyl in 20 ml. of carbon bisulfide was added dropwise 220 mg. of bromine in 5 ml. of carbon bisulfide. After evaporation in a current of carbon dioxide at 25°, the residue was recrystallized twice from ligroin[2]; the yield was 110 mg. The solution of 95 mg. of this crude product in 200 ml. of warm petroleum ether was developed on a 23.5 × 5.3 cm. column with benzene and petroleum ether (1:10).

90 colorless
20 yellow, no fl.: dibromo-terthienyl
10 interzone
15 yellow; no fl.: higher bromination product
100 empty bottom zone

The dibromo compound was eluted with ether, evaporated and crystallized from 4 ml. of ligroin; the yield was 43 mg., m. p. 160–161°. In benzene solution the extinction curve showed a single peak, *viz.*, at 366–367 mμ, where $E^{\text{mol.}}_{1\,\text{cm.}} = 2.60 \times 10^4$.

TABLE II

SOME POLYTHIENYLS: ANALYTICAL DATA

Compound	Empirical formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Sulfur Calcd.	Sulfur Found	Mol. wt. Calcd.	Mol. wt. Found
α-Quaterthienyl	$C_{16}H_{10}S_4$	58.15	58.33	3.05	3.51	38.81	37.81	330	335
α-Terthienyl	$C_{12}H_8S_3$	58.03	57.97	3.25	3.54	38.73	37.70	248	242
2,2′-Bithienyl	$C_8H_6S_2$	57.79	57.99	3.64	4.05	38.57	37.90	166	163
1,10-Dimethyl-α-quaterthienyl	$C_{18}H_{14}S_4$	60.29	59.72	3.94	4.06	...	...	358	336
1-Methyl-α-terthienyl	$C_{13}H_{10}S_3$	59.50	59.22	3.84	3.94	36.66	35.62	262	259
1,8-Dimethyl-α-terthienyl	$C_{14}H_{12}S_3$	60.83	61.12	4.38	4.72	34.79	34.08	276	279
1,8-Dibromo-α-terthienyl	$C_{12}H_6S_3Br_2$	35.48	35.75	1.49	1.58	39.35	39.70	...	...

The analytical data are condensed in Table II. All samples, except bithienyl, were dried in high vacuum, at 56°, for two to four hours and stored *in vacuo*, in darkness. The sulfur was determined according to the Pregl "spiral tube" procedure for non-nitrogenous compounds.[5] Molecular weights were taken by the Rast method, in exaltone (except for quaterthienyl).

Summary

The chromatography of certain α-polythienyls is described and extinction curves are given.

PASADENA, CALIFORNIA RECEIVED AUGUST 10, 1946

[5] H. Roth, "Quantitative Organic Microanalysis of Fritz Pregl," Blakiston, Philadelphia, 1937, p. 116.

[CONTRIBUTION NO. 1080 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

A Blue-fluorescing Compound, Terthienyl, Isolated from Marigolds

BY L. ZECHMEISTER AND J. W. SEASE

It was reported briefly, in collaboration with A. Sandoval,[1] that the yellow petals of the "Lemon" or "African" variety of the common marigold (*Tagetes erecta* L.) contain a substance which shows intense sky-blue or ink-blue fluorescence, both in solutions and in adsorbates. While the greenish-gray fluorescing phytofluene is very widespread in carotenoid-containing vegetable tissues,[1] the knowledge of the occurrence of the blue-fluorescing compound is so far restricted to the variety mentioned.

It was shown earlier that phytofluene is closely related to carotene; indeed, it is a colorless C_{40}-polyene hydrocarbon.[2] In contrast, the blue-fluorescing compound is spectroscopically quite different from the common carotenoids. Furthermore, it does not show any *cis–trans* isomerization[3] or an instantaneous coloration on acid earths.[4] The operations described below led to the isolation of crystals which in the crude state contained 32 to 35% sulfur but were free of oxygen or nitrogen. The analysis of a pure sample (38% sulfur) indicated a heterocyclic aromatic structure, in accordance with the strongly positive indophenine reaction. The sulfur cannot be removed from the molecule by heating with alkaline lead solution, which remains colorless. Likewise negative were tests for sulfhydryl groups. The whole behavior of the compound and the analytical data pointed to the class of the α-polythienyls, $C_4H_3S(C_4H_2S)_n$, C_4H_3S, and the molecular weight, which was found to be near 240, made a comparison with α-terthienyl (mol. wt., 248) advisable.

Since, in spite of Steinkopf's extended studies,[5] neither the quantitative separation of the members of the polythienyl series seemed to be entirely satisfactory for our purposes nor were spectral curves available, we recently made a limited experimental contribution to this field.[6] It was found that, under suitable conditions, polythienyls can be separated easily from each other on the alumina column. In contrast, α-terthienyl is not separable from our marigold compound under similar conditions. Both show a distinctly weaker adsorbability than higher members of the polythienyl series and 1-methyl- or 1,8-dimethyl-α-terthienyl. Furthermore, the natural product and synthetic α-terthienyl do not give any melting point depression.

The spectroscopic data obtained can be summarized as follows: In hexane solution ($\lambda_{max.}$ at 350 mμ) the compound isolated from marigolds

[1] L. Zechmeister and A. Sandoval, *Arch. Biochem.*, **8**, 425 (1945).

[2] L. Zechmeister and A. Sandoval, THIS JOURNAL, **68**, 197 (1946); *cf.* H. H. Strain, *Nature*, **137**, 946 (1936); *J. Biol. Chem.*, **127**, 191 (1939).

[3] For a review of this field, *cf.* L. Zechmeister, *Chem. Rev.*, **34**, 267 (1944).

[4] The behavior of phytofluene was described by L. Zechmeister and A. Sandoval, *Science*, **101**, 585 (1945); the reaction itself was discovered by K. Takahashi and K. Kawakawi, *J. Chem. Soc. Japan*, **44**, 590 (1923).

[5] W. Steinkopf, "Die Chemie des Thiophens," Th. Steinkopff, Dresden, 1941; W. Steinkopf, R. Leitsmann and K. H. Hofmann, *Ann.*, **546**, 180 (1941).

[6] J. W. Sease and L. Zechmeister, THIS JOURNAL, **69**, 270 (1947).