nants and consumes about 25% of the yield of phthalocyanine. Thorough washing after sulfuric acid treatment will give a product with only 0.05% ash. This low-ash, metal-free phthalocyanine has proved to be the most suitable material for lubrication purposes.

Ordinary solvents do not dissolve phthalocyanine, but it has slight solubility in chlorinated aromatic compounds, such as trichlorobenzene. Metal-free phthalocyanine can be purified by recrystallizing it from concentrated sulfuric acid. Strong chemical oxidizing agents will decompose it, but it is not affected by nonoxidizing acids, alkalies, or mild oxidants.

The stability of the compound to radiation is good. Data on neutron irradiation showed only 0.05% decomposition in 100 hours at 2×10^{13} neutrons per sq. cm. per second. Gaseous products were methane, hydrogen, and nitrogen. Phthalocyanine also proved to be stable to gamma radiation.

Semiconductor properties have been observed for phthalocyanine, and this activity can be ascribed to mobile pi electrons in the structure. Conductivity has been shown to be a linear function of the applied field.

CONCLUSIONS

Experimental data have been presented which demonstrate that metal-free phthalocyanine is a potential lubricant for extreme conditions of load and temperature. For the conditions under which the experiments were performed, metal-free phthalocyanine is most efficient as a lubricant in the temperature range of 800° to 1350° F. The phthalocyanine may be capable of lubrication at temperature in excess of 1350° F.

Although precise mechanisms of lubrication with phthalocyanines are not known at this time, it is believed that lubrication processes are similar to those which occur with other planar structure, solid lubricants, and that strongly adherent and protective lubricating films are formed by chelation of metal-free phthalocyanine with metal substrates. The apparent lack of lubrication provided by metallated phthalocyanines—for example, copper phthalocyanine—appears to support this concept of a lubricant film attached by chemical reaction to the substrate.

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LITERATURE CITED

(1) Cosgrove, S.L., Sibley, L.B., Allen, C.M., "Evaluation of Dry Powdered Lubricants at 1000° F. in a Modified Four-Ball Wear Machine," Am. Soc. Lubrication Engrs. Conf., Buffalo, N. Y., April 1959.

(2) Ebert, A.A., Gottlieb, H.B., *J. Am. Chem. Soc.* **74**, 2806 (1952).

(3) Glaeser, W.A., Allen, C.M., WADC Tech. Rept. **59-179** (April 1959).

(4) Sibley, L.B. Allen,C.M., others., *Ibid.*, **TR-59-790** (June 1960).

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Synthesis and Investigation of Polynuclear Alkyl-Polyphenyl Hydrocarbons as Potential High Temperature and Radiation-Resistant Fluids

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THE OBJECTIVE of the research program conducted at the University of Denver's Research Institute (*15*) was to investigate the feasibility of polynuclear aromatic compounds as potential high-temperature and radiation-resistant materials and to alter the molecular structure of the most promising representatives of this class of compounds in such a way as to improve their liquid range and lubricity with the least loss in thermal, oxidative, and radiation stability.

Promising compounds of this class were biphenyls, and low molecular weight polyphenyls such as terphenyls and quaterphenyls. The parent compounds of these classes have in themselves remarkable thermal stability, and it was therefore expected that a careful investigation of this group would lead to derivatives meeting the requirements of the Air Force.

A rather comprehensive literature survey of polyphenyl compounds and their derivatives revealed a series of biphenyl, terphenyl, and quaterphenyl compounds with high boiling points and sufficiently low melting points to suggest their use as starting materials for the synthesis of derivatives with more desirable properties.

DISCUSSION

A survey of the literature showed that the influence of the chemical structure of the parent compounds, as well as that of the substituents, on physical properties, particularly melting or pour points, can be summarized as follows:

The melting point (or pour point) of the polyphenyl compounds or their derivatives is in general higher if the over-all symmetry of the compound is high and is lower whenever this symmetry is reduced by change in structure of the parent compounds or the introduction of substituents.

This correlation becomes evident among the parent *p*-terphenyl isomers; linear compounds, linked in the *p,p* position, show the highest melting points and highest boiling points; isomers linked in the ortho or in the meta position show comparatively lower melting points than the linear configurations.

Melting points and boiling points of the polyphenyl derivatives are altered by such factors as: position of substituents, length of substituent or side chain, symmetry of side chain, type of substituent, and number of substituents. Among these factors, the position of the substituent has the greatest influence on the depression of the melting point—2- or 3-alkyl-biphenyls melt at much lower temperatures than the corresponding 4-substituted compound.

Based on the literature survey and consideration of physical and chemical requirements such as boiling range, viscosity, lubricity, and thermal and radiation stability, it appeared that the most promising compounds among the polyphenyls would be alkyl and ether derivatives of such parent compounds as biphenyls, terphenyls, and eventually quaterphenyls; emphasis was subsequently placed on the investigation of alkyl derivatives.

From the experimental results of an exploratory synthesis program including such compounds as 4-isopropyl-*m*-terphenyl and other alkylterphenyls, it appeared that a detailed investigation of various alkyl-*m*-terphenyl series would be a feasible way to obtain liquids with the desired properties. Two series of compounds were of interest: compounds with substitution of various alkyl groups of definite structure at the same position of the terphenyl molecule for which the 4′-alkyl-*m*-terphenyl derivatives were chosen, because of expected melting point depressions, availability of starting material, and ease of synthesis; and compounds with the same alkyl group at different positions on the terphenyl nucleus for which the *n*-heptyl series was selected.

The preparation of alkyl polyphenyl derivatives of specific structure was also of great interest because of the potential use of polyphenyls and their derivatives as radiation-stable materials (*14*).

It is known that aromatic and/or polyaromatic hydrocarbons such as benzene or biphenyl have greater radiation stability than aliphatic and/or alicyclic hydrocarbon compounds of comparable molecular weight, and it is generally assumed that this stability is connected with the strongly resonating nature of the aromatic structure which will allow for a rapid energy dissipation in the molecule, other than by bond rupture, thus reducing the degree of degradation and/or polymerization.

Similar phenomena have been observed with naphthalene, terphenyls, and polyphenyl ethers; indeed these exhibit even higher radiation stability than benzene. The latter two groups of compounds have considerable interest as base materials for radiation stable organic fluids and/or reactor coolants.

Earlier investigations (*3–5, 12*) have also shown that aromatic hydrocarbons such as benzene or polyphenyls, etc., when in mixtures with aliphatic or alicyclic hydrocarbons such as *n*-hexane or cyclohexane, will protect the latter to some extent against radiolysis from the energy of ionizing radiation. This protective effect has been attributed to an energy transfer from the less stable molecule to the more stable molecules. Because of the lower excitation and ionizing potentials of the aromatic compounds as compared with those of cyclohexane, for example, it is possible that such transfer may be energetically operative.

This protective role of a resonating structure in reducing the radiolytic degradation of an aliphatic system was of particular interest in the study of the properties of alkylpolyphenyl hydrocarbons. The effects of direct attachment by covalent bonding of the alkyl constituent to the resonating system were of special interest. Assuming a greater probability of an energy transfeı from the activated side chain to the resonant system, the rate of energy transfer and dissipation could be sufficiently fast to prevent or lessen the degree of alkyl chain degradation. If this is the case, then it is of interest to study the effects of length and position of the alkyl side chain on the aromatic molecule and also the effects of aromatic isomerism on the radiolytic stability of the molecule. Such studies are valuable in establishing the possible breakdown mechanism for these compounds. This research program was therefore undertaken and is still in progress.

The literature on the subject of radiation effects of organic compounds in general had been surveyed and reviewed more recently by various workers in the field (*6, 11, 18*). A general review of the subject as related to hydrocarbons has been covered by Schmidt and others (*14*). Other recent publications related directly to alkyl aromatic hydrocarbons are those by Gordon (*9*) and Wagner (*19*).

EXPERIMENTAL

Synthesis. Several methods of preparing alkylpolyphenyl derivatives have been used. Of these the following have been applied successfully or appeared to have merit as far as the preparation of specific polyphenyl compounds (having reasonable yields) was concerned.

FRIEDEL-CRAFTS REACTION. The direct alkylation of biphenyl or terphenyls with alkyl halides in the presence of aluminum chloride gave alkylbiphenyls or alkylterphenyls. The structure of the product was, however, somewhat uncertain, as Friedel-Crafts alkylations are known to give both mono- and polyalkylation as well as rearrangement of the alkyl group and of the terphenyl nucleus. A typical example of this type of synthesis is the alkylation of *m*-terphenyl with isopropyl bromide. According to the conditions used, products were obtained which were shown to contain from one to four isopropyl groups per molecule of *m*-terphenyl, on the basis of molecular weight analysis. Therefore this method was used mostly for exploratory synthesis and for the preparation of mixed isomeric compounds. Whenever a monosubstituted alkyl derivative was prepared, substituion occurred in the 4-position.

Biphenyl and terphenyls were also acylated with acid chlorides to give the 4-acyl derivatives, the keto group then being reduced to give the desired alkylbiphenyl or alkylterphenyl.

PREPARATION FROM HALOGENATED POLYPHENYLS. The halogenated biphenyls or terphenyls were converted into the corresponding lithium compounds by reaction with *n*-butyllithium. The lithium compounds were reacted with selected aldehydes or ketones to give alcohols which were dehydrated to alkenylbiphenyls or alkenylterphenyls. These compounds were selectively hydrogenated to the desired alkylbiphenyls or alkylterphenyls. The 4′-alkyl-*m*-terphenyl series is a typical example of this method of synthesis. The starting material for this synthesis, 4′-bromo-*m*-terphenyl, was obtained from the direct bromination of *m*-terphenyl (*16*).

PREPARATION OF TERPHENYLS FROM BIPHENYLYLLITHIUM COMPOUNDS. For the preparation of 3-alkyl-*m*-terphenyls, 3-biphenylyllithium was reacted with the desired 3-alkylcyclohexenone (obtained from the reaction of the alkyl magnesium halide with the ethyl enol ether of dihydroresorcinol). The resulting alkylbiphenylylcyclohexenol was dehydrated to the cyclohexadiene, which in turn was dehydrogenated to the 3-alkyl-*m*-terphenyl. By this method, the use of 2- or 4-biphenylyllithium leads to 3-alkyl-*o*-terphenyls or 3-alkyl-*p*-terphenyls.

In similar manner, a 2-alkylcyclohexanone was reacted with the appropriate biphenylyllithium compound to form a 2-alkyl-*o*-, -*m*-, or -*p*-terphenyl.

In the above syntheses, the corresponding Grignard reagent was often as satisfactory for the preparation of the desired compound.

Physical Properties. Various physical properties of the synthesized compounds were determined and correlated with chemical structure—particularly with portion of the alkyl chain on the parent molecule—chain length, and branching. The physical properties of the synthesized alkyl derivatives followed the general pattern of the literature data. The compounds of the 4′ series were investigated in greater detail with respect to the influence of chain on length and branching, and it was assumed that similar correlations will prevail with alkyl derivatives substituted in other positions. The physical properties of these compounds have been used to guide further the preparations of alkyl compounds substituted in other positions of the terphenyl molecule.

The more significant physical property data of a number of alkylbiphenyls and alkylterphenyls are summarized in Table I. The interpretation of these data can be summarized as follows:

MELTING POINT AND POUR POINT. Melting and pour points of homologous *n*-alkyl derivatives decrease with increasing chain length and pass through an apparent minimum when the chain length is in the order of 11 to 13 carbon atoms. Pour point values alternate with number of carbon atoms, the odd-numbered alkyl derivatives having the lower pour points. Symmetrically or asymmetrically branched derivatives show higher pour points than the corresponding *n*-alkyl compounds.

From previously mentioned correlations it was to be expected that substitution in the 3 and/or 2 position of the *m*-terphenyl molecule would result in a further drop of the pour point, as compared with the corresponding 4′ substitution. Therefore several 3-alkyl-*m*-terphenyls were synthesized having the same number of C atoms in the side chain as the 4′ derivatives. The 3-substituted compounds such as 3-*n*-heptyl, 3-*n*-amyl, or 3-*n*-propyl-*m*-terphenyl have pour points which are 10° F. lower than the corresponding 4′ analogs. Substitution in the 2 position should cause similar depression of the pour point; however, it was not as large with longer alkyl chains as originally expected, probably because of increased steric hindrance.

VISCOSITY. Viscometric properties of various alkyl derivatives of biphenyl and terphenyls are presented in Table I.

Thermal Stability. There is no one method which gives a very reliable measure of thermal stability. Three tests were used in an effort to establish some measure of this property of the compounds prepared: the measurement of vapor pressure in the isoteniscope, a prolonged heating in an inert atmosphere, and a distillation in air at the prevailing atmospheric pressure. The last method is also a measure of oxidative stability.

Table I. Physical Properties of Alkylbiphenyls and Alkylterphenyls

Alkyl Group	Position of Substitution	B.P., ° C.	Mm.	n_D^{20}	Pour Point, ° F.	Viscosity, Cs. 100° F.	Viscosity, Cs. 210° F.	ASTM Slope
			Biphenyls					
n-C_7H_{15}-	2	126[a]	0.3	1.5589[c]	−65	6.99	1.85	0.90
n-C_7H_{16}	3	156	0.4	1.5704[c]	−80	9.90	2.32	0.87
n-C_7H_{15}-	4	144	0.5	1.5538[c]	[b]	8.41	2.31	0.80
			o-Terphenyls					
n-C_7H_{15}-	2	163	0.3	1.5682[c]	15	129	6.55	1.00
n-C_7H_{15}-	3	167	0.3	1.5652[c]	−10	55.2	5.14	0.93
			m-Terphenyls					
iso-C_3H_7-	4	185	0.8	1.6222–30	20	139	6.77	1.00
(*iso*-C_3H_7)$_4$-		217	0.5		90		6.77	1.00
n-C_3H_7-	3	179	0.6		5			
n-C_5H_{11}-	3	200	0.7	1.6002[c]	−5			
n-C_7H_{16}-	2	170	0.3	1.5803[c]	30	173	7.61	0.99
n-C_7H_{15}-	3	215	0.9	1.5760[c]	−20	65	6.29	0.85
n-C_7H_{15}-	4	188	0.5		[d]	65	6.29	0.85
n-C_3H_7-	4′	153	0.3	1.6204	20			
n-C_5H_{11}-	4′	203	1.2	1.6050[c]	5			
n-C_6H_{13}-	4′	208	1	1.6141[c]	25			
n-C_7H_{15}-	4′	194	0.4	1.5921	−10	64.9	6.18	0.86
n-C_9H_{19}-	4′	213	0.6	1.5781	−15	64.7	7.07	0.79
n-$C_{11}H_{23}$-	4′	219	0.5	1.5590	−25	64.4	7.62	0.76
n-$C_{12}H_{25}$-	4′	232	0.4	1.5675[c]	−10			
Cyclohexyl-	4′	196	0.5		[e]			
$(C_2H_5)_2CH$-	4′	164	0.3	1.6203	60			
(*n*-C_3H_7)$_2$CH-	4′	185	0.6	1.6109	10			
(*n*-C_4H_9)$_2$CH-	4′	182	0.3	1.5953	35	395	11.8	0.95
(*n*-C_5H_{11})$_2$CH-	4′	194	0.3	1.5749	20	246	10.1	0.94
(*n*-C_6H_{13})$_2$CH-	4′	199	0.2	1.5641[c]	50			
(C_2H_5)(*n*-C_4H_9)CH-	4′	169	0.3	1.5938	45			
(CH_3)(*n*-C_6H_{13})CH-	4′	184	0.3	1.5944	20			
(CH_3)(*n*-$C_{15}H_{31}$)CH-	4′	241	0.2		[f]			
			p-Terphenyls					
n-C_7H_{15}-	2	216	0.7		40	110	7.03	0.93
n-C_7H_{15}-	3	[g]			[h]			
n-C_7H_{15}-	4	[g]			[i]			

[a] All boiling points and melting points are uncorrected. [b] M.p. 23° C. [c] n_D^{25}. [d] Not determined, liquid at room temperature. [e] M.p. 75–76° C. [f] M.p. 45° C. [g] Purified by recrystallization. [h] M.p. 74–75° C. [i] M.p. 150°–152° C.

The Isoteniscope. Two types of isoteniscopes were used, the classical Smith-Menzies type (*17*) and the Greene type (*10*). In both types, increasing the vapor pressure of the compound being tested as the temperature is raised unbalances the liquid levels in a U-tube manometer (Smith-Menzies) or forces liquid from a capillary (Greene). The external pressure necessary to balance the liquid levels is taken as the vapor pressure at that temperature.

The measurement of thermal stability in the isoteniscope seems to give reliable values, if the compound being investigated is thermally stable up to temperatures close to the boiling point of the compound. For such compounds the plot of $1/T$ °A *vs.* the logarithm of the vapor pressure is a straight line and thus hardly subject to various interpretations. However, if the compound is not thermally stable up to those temperatures, the data obtained do not give a straight line plot or a sharp nick point as would be expected and are subject to various interpretations, frequently of questionable value.

Figure 1 shows results obtained from the isoteniscope study of a thermally stable compound, isopropyl-*m*-terphenyl. Both types of isoteniscopes gave identical vapor pressure curves until high temperatures were reached. Whereas the Smith-Menzies type isoteniscope showed no deviation from a straight line, in another run a Greene-type isoteniscope showed a definite break in the curve at 400° C. Edwards, Blake, and Hammann (*2*) have reported a decomposition point of 396° C. for isopropyl-*m*-terphenyl from an isoteniscope study.

Figure 2 shows results obtained for a somewhat less thermally stable compound, 4′-*n*-amyl-*m*-terphenyl.

Several 4′-alkyl-*m*-terphenyls, some of which were known to be thermally unstable from direct distillations in air (notably 4′-*n*-dodecyl-*m*-terphenyl) were studied in both types of isoteniscopes. Figure 3 shows the behavior of a typical thermally unstable compound, specifically 4′-*n*-dodecyl-*m*-terphenyl, run in a Greene-type isoteniscope. The obvious and definite conclusion is that the plot is not a straight line. Two straight lines of different slopes can be drawn through selected points from this experiment.

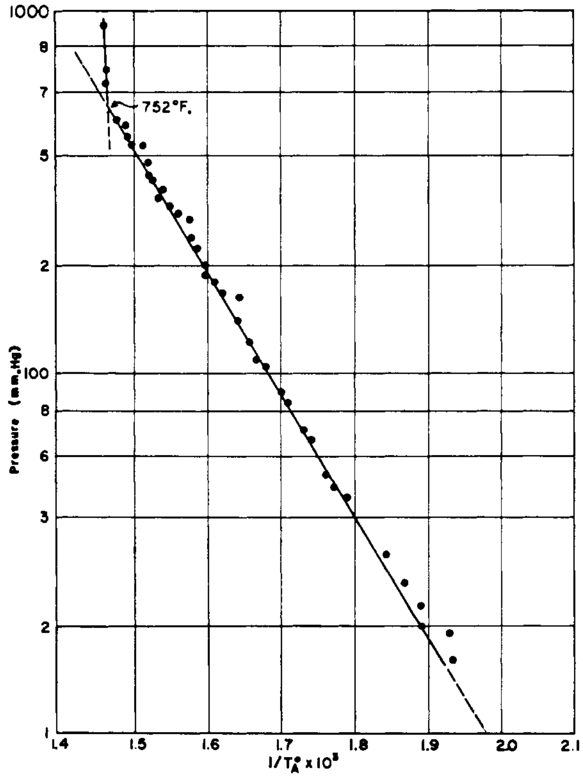

Figure 1. Isoteniscope curve of isopropyl-*m*-terphenyl

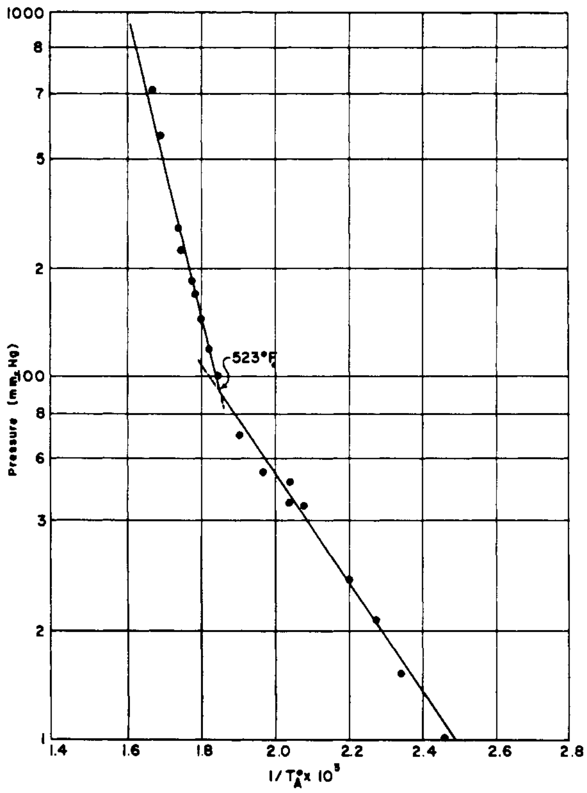

Figure 2. Isoteniscope curve of 4′-*n*-amyl-*m*-terphenyl, run 2

The line drawn through points at lower pressures may represent the vapor pressure of the undecomposed 4′-*n*-dodecyl-*m*-terphenyl.

Extrapolation of this line to 760 mm. gives a boiling point of 417° C., which is a reasonable value for such a compound. The straight line drawn through points at higher pressure may represent the vapor pressure of the residue after decomposition has occurred and the lower boiling material was removed. In a different determination, that for the vapor pressure of 4′-(1-methylhexadecyl)-*m*-terphenyl, the isoteniscope containing the decomposition residue was cooled and the vapor pressure was redetermined. The new vapor pressure values fell on the extension of the line through the higher vapor pressure values of the initial determination. It is believed that the last point on the line through the lower vapor pressure values may represent the last point of definite thermal stability. For 4′-*n*-dodecyl-*m*-terphenyl, this value is 222° C.

The other members of the 4′-alkyl-*m*-terphenyl series tested—namely, the *n*-heptyl, (1-methylheptyl), and (1-methylhexadecyl) derivatives—were of about the same thermal stability as 4′-*n*-amyl-*m*-terphenyl (Figure 2).

Heating in an Inert Atmosphere. Samples were heated for 24 hours at 370° C. in an atmosphere of nitrogen using an apparatus which allowed low boiling decomposition products to be removed from the heated area (*2*). Some of these low boiling products were condensed and retained in the system, whereas others were lost. At the end of the heating period, the sample was examined for changes in weight, refractive index, viscosity, and appearance. Isopropyl-*m*-terphenyl is a very satisfactory heating bath fluid.

Isopropyl-*m*-terphenyl was heated in a nitrogen atmosphere for 24 hours at 380° to 387° C. and for an additional 5 hours at 393° C. At the end of this heating period, the sample was very slightly colored, n_D^{25} had changed from 1.6238 to 1.6232 and the 100° F. viscosity from 139 to 138 cs.

In the 4′-alkyl-*m*-terphenyl series, typical weight losses

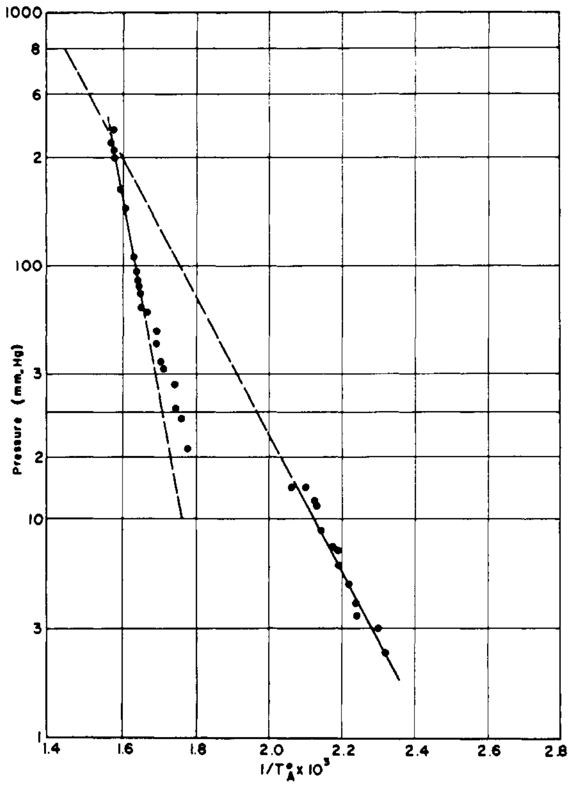

Figure 3. Isoteniscope curve of 4′-*n*-dodecyl-*m*-terphenyl

(from the system) ranged from 3 to 8%. After the test period, the residues remaining in the heated area were usually slightly colored. Ocasionally a sample became very dark. It is believed that, for these samples, the low boiling material may have polymerized before it was removed from the heated area. In some cases impurities in the sample such as traces of residual halogen derivatives contributed to discoloration and faster deterioration.

DISTILLATION IN AIR. Small samples were distilled in air at the prevailing atmospheric pressure. Relatively stable alkylterphenyls, such as isopropyl-*m*-terphenyl and tetraisopropyl-*m*-terphenyl distilled at approximately 390° C. at 630 mm. and 420° C. at 634 mm. of mercury, with only slight coloration of the distillate and residue. Thermally unstable polyphenyl compounds, such as certain members of the 4′-alkyl-*m*-terphenyl series, decompose when similarly treated.

Thermal decomposition during distillation is particularly evident for 4′-alkyl-*m*-terphenyls with more than seven carbons in the alkyl group. On distillation of such compounds in air at normal pressures, decomposition occurred, sometimes at a temperature as low as 280° C. to give a low boiling distillate which on the basis of infrared spectra analysis and characteristic odor is tentatively identified as an aliphatic olefin. After removing the low boiling material, the residue can be distilled in a boiling range between that of *m*-terphenyl and that of the alkyl-*m*-terphenyl compound with no evidence for further decomposition. No definite compounds have been isolated from the residue.

In addition to the above tests, isopropyl-*m*-terphenyl was heated in an atmosphere of air for 6 hours at 395° C. At the end of this time, the sample had become colored with considerable charring at the air interface and the viscosity had increased from 139 to 266 cs. at 100° F.

Lubrication Tests. From the evaluation of physical properties and thermal stabilities of various alkylbiphenyl and alkylterphenyl compounds, it appeared that the optimum compromise between boiling point, liquid range, viscosity properties, and thermal stability in the alkypolyphenyl series, may be straight-chain alkyl-*m*-terphenyl derivatives with substitution in the 3 position or the 4′ position with an odd number of carbon atoms, 11 or less, in the alkyl side chains.

Subsequently, 0.5-gallon quantities each of 3-*n*-heptyl-*m*-terphenyl and 4′-*n*-nonyl-*m*-terphenyl and 1 gallon of 4-isopropyl-*m*-terphenyl (the thermally most stable of the alkyl series) were prepared and submitted to the Materials Laboratory, Wright Air Development Center, for the Shell 4-ball wear test.

Results of lubrication tests on alkylterphenyl derivatives and comparisons with other alkylpolyphenyls as well as with aryl ethers are presented in Table II (Courtesy Wright Air Development Center, Materials Laboratory, Lubricants Section). These data reflect the detrimental effect of aromatic or polyaromatic nuclei in the molecule of the liquid on lubrication properties at higher loads. It becomes most evident in isopropyl-*m*-terphenyl. The polyphenyl and polyaryl ether compounds substituted with longer alkyl side chains are somewhat better, although still not as good lubricants as the dibasic acid esters or mineral oil lubricants. Aryl ethers show better lubricating properties than the alkylpolyphenyl compounds.

Radiation Stability. METHODS. The effects of gamma irradiation on the hydrocarbons listed in Table III were studied. The purest available compounds as determined by boiling point, melting point, refractive index, density, and gas chromatography were used in the irradiations.

Compounds were prepared for irradiation by either of two methods: In vacuum irradiations the samples were deaerated by repeated freezing under continuous pumping and finally sealed in the glass cells under vacuum or argon, and in oxygen atmosphere irradiations, the samples were deaerated as above followed by saturation with oxygen and sealing in the glass cells in air at the prevailing pressures. The samples were then placed in the Co^{60} source and irradiated to the indicated doses at a rate of about 4.5×10^5 r. per hour.

After irradiation, the gases were collected, their volumes were measured, and they were analyzed on a gas chromatograph. Physical properties were determined on the liquid phase. A Beckman GC-2 gas chromatograph was used for the analysis of compounds and yield components boiling up to about 300° C. For higher boiling materials, a high-temperature gas chromatograph was utilized. This chromatograph was modified from the basic design of Felton (*8*) and is functional to 350° C. column temperature with such column partitioning materials as polyethylene, silicone grease, asphaltenes (*13*), and polyphenyl tar (*1*).

The liquid phase was further studied by normal and differential ultraviolet and infrared spectroscopy. Certain separations were also affected by the use of countercurrent distribution methods. The countercurrent distribution separations were particularly useful in removing yield polymers from the target material.

Table II. Shell 4-Ball Wear for Several Alkylated Terphenyls

Conditions. 400° F., 600 r.p.m., 1 hour, M-10 balls, wear scar measured in mm.

Fluid	Load, Kg. 4	10	40
Bis(2-ethylhexyl) sebacate (Plexol 201)	0.34	0.38	0.92
1-Methylheptadecyl diphenyl ether	0.31	0.48	0.92
Bis(*p*-phenoxyphenyl) ether	0.68	1.00	1.26
4′-*n*-Nonyl-*m*-terphenyl	0.47	0.52	2.32
3-*n*-Heptyl-*m*-terphenyl	0.47	0.57	2.12
Tetraisopropyl-*m*-terphenyl	0.53	0.60	1.91
4-Isopropyl-*m*-terphenyl[a]	0.44	0.67	3.70+

[a] Run at 167° F., 1200 r.p.m., 2 hours, with 52-100 balls.

Micromolecular weights were determined by methods described by Dimbat (*7*).

Discussion of Results. The data given in Table III show very clearly the effects of a resonant structure on the radiation stability of hydrocarbons of nearly the same molecular weight—i.e., hexane, cyclohexane, and benzene. The radiolysis of hexane gives high gas yields and large G_m values. The yield products are predominantly of higher molecular weight than hexane, with a rather large amount of unsaturated aliphatic material present. This indicates that C—H bond scission prevails over C—C bond scission. Radiolysis of cyclohexane indicates a predominance of C—H scission. Bicyclohexyl ($G = 0.47$) and hexylcyclohexane ($G = 0.12$) were identified in the yield products.

The irradiation of benzene shows the effects of resonance on radiation stability by lowered gas yields and G_m values as compared to the above compounds. A yield product not previously reported shows by infrared a predominance of 1:2 aromatic substitution. This material slowly sublimes above 250° C. and is tentatively assumed to be a mixture of *o*-polyphenyls of greater molecular weight than terphenyl.

The yield values from heptylbiphenyls (Table III. compounds 6, 7, and 8) show the effects of an increased amount of resonance in the molecule on stability as compared to hexylbenzene. These data (*G* values and viscosity changes) also indicate an effect of the alkyl chain position on compound stability. The 4 position appears to be much more stable than the sterically hindered 2 position. Beside the gaseous products and trace amounts of benzene, the significant yield products detected by gas-liquid phase chromatography and verified by infrared spectroscopy were the cis and trans form of a 2-heptenylbiphenyl. The trans isomer is formed in considerably greater yields than the cis form; G trans $= 0.024$, G cis $= 0.008$. Only a small amount of trans olefin (no cis) was found in the infrared spectrum of the 4-heptylbiphenyl; none was detected by GLPC methods.

Further examination of the data in Table III concerning the alkylterphenyls shows insignificant differences in the stabilities of these compounds as measured by various yield values. The 2-heptyl-*m*-terphenyl changed least in viscosity and remained almost colorless during irradiation, whereas the other compounds became yellow or light brown.

A countercurrent distribution separation of the 3-heptyl-*o*-terphenyl (No. 11, Table III) yielded a fraction which, by infrared spectroscopy, showed a saturation of the ring bearing the alkyl chain. This fraction also boils higher than the original hydrocarbon as indicated by GLPC. This is indicative of the greater radiolytic susceptibility of an aromatic ring bearing an alkyl chain as compared to a nonalkylated aromatic ring.

A series of irradiations was made with 4′-heptyl-*m*-terphenyl, the results of which are shown in Table IV. These data show the compound to be rather stable to high radiation doses. The degree of stability is also related very closely to the purity of the original compound—i.e., No. 6, Table IV, and No. 11, Table III, contained a small amount of impurities before irradiation and consequently produced the highest G_m values. Viscosity changes of the 4′-heptyl-*m*-terphenyl are shown to be almost a linear function of irradiation dose.

Table III. Viscosity Changes and Yield Values of Irradiated Hydrocarbons

	Compound	Dose, 100 E.V. × 10^{-22}	Viscosity Change, %		*G* Values, Molecules Formed per 100 E.V. Energy Absorbed			
			100° F.	210° F.	G_{gas}	G_{H_2}	G_{CH_4}	$-Gm^a$
1	Hexane	0.086	14.9 (0° F.)	5.9 (100° F.)	3.54	2.73	0.23	9.9
2	Cyclohexane	0.128	4.3	...	4.18	4.14	0.04	16.0
3	Benzene	0.180	...	...	0.068	0.055	0.010	1.2
4	*n*-Butylbenzene	0.172	...	...	0.207	0.167	0.011	0.76
5	*n*-Hexylbenzene	0.643	8.5 (0° F.)	8.05 (100° F.)	0.685	0.250	0.031	7.9
6	2-*n*-Heptylbiphenyl	0.208	4.5	4.6	...	...	...	1.64
7	2-*n*-Heptylbiphenyl	1.27	20.48	15.14	0.095	0.092	0.0011	1.31
8	4-*n*-Heptylbiphenyl	1.98	8.0	6.0	0.062	0.0606	0.0063	0.31
9	3-*n*-Propyl-*o*-terphenyl	0.281	3.05	2.90	0.030	0.0280	0.0010	0.89
10	3-*n*-Heptyl-*o*-terphenyl[b]	0.324	14.5	10.5	0.035	0.033	0.0007	0.401
11	3-*n*-Heptyl-*o*-terphenyl[b]	0.517	24.5	8.1	0.112	0.1093	0.0016	1.68
12	4′-*n*-Propyl-*m*-terphenyl	0.301	10.1	2.0	0.0195	0.0186	0.0003	−0.52
13	4′-*n*-Heptyl-*m*-terphenyl	0.565	12.3	4.8	0.076	0.0740	0.0020	0.78
14	4′-*n*-Heptyl-*m*-terphenyl	1.530	28.5	15.1	0.054	0.0506	0.0021	0.38
15	4′-*n*-Nonyl-*m*-terphenyl	0.245	22.6	−4.0	0.049	0.0454	0.0016	0.73
16	2-*n*-Heptyl-*m*-terphenyl	0.380	6.9	2.8	0.0723	0.0698	0.0009	0.44
17	2-*n*-Heptyl-*p*-terphenyl	0.273	14.1	12.5	0.050	0.047	0.0020	0.55

[a] Molecules of target destroyed per 100 e.v. energy absorbed.

[b] Nos. 10 and 11 are from different synthesis, No. 10 is the pure compound.

Table IV. Physical Property Changes and Yield Values of Irradiated 4′-*n*-Heptyl-*m*-terphenyl

Sample Number	Dose, 100 E.V. × 10^{-22}	Viscosity Change, %		Density Change, G./Ml.	n_D^{20} Change Unit	*G* Values, Molecules Formed per 100 E.V. Energy Absorbed			
		100° F.	210° F.			G_{gas}	G_{H_2}	G_{CH_4}	G_m^a
1	0.0011	−2.29	−2.43	−0.0023	0.0	0.073	0.073	0.0	...
2	0.012	4.12	−0.93	−0.0001	0.0009	0.045	0.045	Trace	...
3	0.130	6.68	1.94	0.0013	0.0010	0.058	0.0527	0.0026	0.49
4	0.565	12.33	4.80	0.0037	0.0013	0.076	0.0740	0.0020	0.78
5	1.270	25.10	11.62	0.0036	0.0020	...	...	...	1.18
6[b]	0.590	4.39	1.28	0.0037	0.0035	0.084	0.0810	0.0016	2.42
7[c]	0.162	3.09	0.0	0.0022	0.0004	0.045	0.0410	0.0020	0.70
8	1.530	28.5	15.1	0.0025	0.0036	0.054	0.0506	0.0021	0.38

[a] Molecules of target destroyed per 100 e.v. energy absorbed.

[b] All material was from the same synthesis except No. 6.

[c] All material was irradiated under vacuum, except No. 7 which was irradiated in air atmosphere.

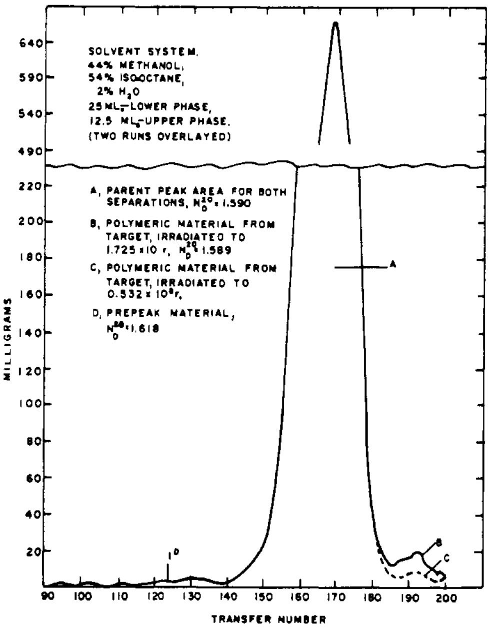

Figure 4. Countercurrent distribution separations of irradiated 4′-heptyl-*m*-terphenyl

Samples 3 and 4, Table IV, were subjected to a countercurrent distribution separation as shown in Figure 4. The material found under area *D* (Figure 4) had an average molecular weight of 286 indicating the material must be scission products with very small fragments of alkyl chains on the parent terphenyl molecule. The area under band *C* shows an increase with irradiation dose and an average molecular weight of 903. This molecular weight indicates the material must be predominantly a trimer of the original hydrocarbon. Infrared spectra of these fractions are almost identical to those of the parent compound. It was concluded from this that polymeric material was isolated and that polymerization had occurred through the alkyl chains of the parent material.

It is evident that, as a class, pure species of polynuclear alkylpolyphenyl hydrocarbons are stable to gamma irradiations. It has been shown that, at least in certain compounds, the degree of stability is related to the steric freedom of the alkyl chain. The alkyl chain also renders the aromatic ring to which it is attached more susceptible to radiolytic reactions. Polymerization is responsible for the observed viscosity increases, and it appears to be the greatest radiolytic change occurring in these hydrocarbons. It appears to occur primarily through reactions in the alkyl chain.

Any compound's stability is directly dependent on the purity of the compound. In many cases such criteria as melting point, boiling point, refractive index, etc., are not sufficient to establish purity. Discriminating use of these parameters coupled with spectroscopy and efficient gas chromatography is needed to verify the purity of a material for irradiation studies.

The stability of alkylaromatic hydrocarbons compares very favorably with the stability of another class of stable fluids being studied at present, the polyaryl ethers. The hydrocarbons have higher gas yields than the ethers, but change less in viscosity. The G_m values are nearly the same. The ethers change much more in color and yield considerable polymeric material. They also yield rather large amounts of phenolic materials (up to 1%) which may make them more susceptible to certain in-use deterioration—i.e., thermal, oxidation, and corrosion deterioration —than the alkylaromatic hydrocarbons.

SUMMARY

The liquid range of thermally and radiation stable polynuclear aromatic compounds such as biphenyl and terphenyl can be substantially widened by alkylation and by isomerization of the phenyl nuclei. The greatest depression of the melting point (and simultaneous retention of high boiling point) can be achieved by the substitution of the ortho-terphenyl molecule in the 3 position with a straight-chain alkyl radical containing 11 carbon atoms. The resulting alkyl derivative should have a liquid range from around -20° F. to about 840° F. at normal pressure.

The improvement of the liquid range and lubricity by selective alkylation or other changes in the molecular structure of the parent molecule is, however, associated with some sacrifices in other desirable properties such as thermal and oxidation stability and resistance to ionizing radiation. By judicious choice of the type of alkyl substituents, position of substitution, and type of parent polyphenyl nucleus a number of compounds with varying liquid ranges and varying thermal and radiation stabilities can be derived.

The best compromise between the various desirable properties within this class can be attained in the 3-heptyl-*m*-terphenyl and the 4′-heptyl-*m*-terphenyl derivatives.

While the presence of the alkyl side chain improves considerably the viscometric and lubrication properties of the parent polyphenyl compounds, these derivatives fall short with respect to the latter when compared with other aliphatic hydrocarbon- or ester-type lubricants or with aryl ethers; and their oxidation stabilities leave much to be desired. These compounds have a liquid range from about -20° to 800° F., and may be thermally stable up to 700° F. for long periods of time in spite of a rather long alkyl chain. They show a remarkable radiation stability to high intensity gamma radiation, comparing favorably with other types of radiation-stable organic fluids.

LITERATURE CITED

(1) Baxter, R.A., Keen, R.T., *Anal. Chem.* **31**, 475 (1959).
(2) Blake, E.S., Edwards, T.W., Hammann, W.C., WADC Tech. Rept. **54-532** (1955).
(3) Burton, Milton, Chang, J., Lipsky, S., Reddy, M.P., *Radiation Research* **8**, 203 (1958).
(4) Burton, Milton, Gordon, S., Hentz, R.R., *J. chim. phys.* **48**, 190 (1951).
(5) Burton, Milton, Lipsky, S., *J. Phys. Chem.* **61**, 1461 (1957).
(6) Collinson, E., Swallow, A.J., *Chem. Revs.* **56**, 471 (1956).
(7) Dimbat, Martin, Stross, F.H., *Anal. Chem.* **29**, 1517 (1957).
(8) Felton, H.R., Intern. Gas Chromatography Symposium, Instr. Soc. Am., East Lansing, Mich., August 1957.
(9) Gordon, Sheffield, Van Dyken, A.R., Doumani, T.F., Preprint, Petroleum Division, ACS Meeting, New York, September 1957.
(10) Greene, S.A., *Anal. Chem.* **28**, 428 (1956).
(11) Kinderman, E.M., WADC Tech. Rept. **57-465** (1957).
(12) Krenz, F.H., *Nature* **176**, 1113 (1955).
(13) Ogilive, J.L., Simmons, M.C., Hinds, G.P., *Anal. Chem.* **30**, 25 (1958).
(14) Schmidt, J.J.E., Bohner, G.E., Gray, D.N., WADC Tech. Rept. **58-377** Part 1-2 (1958-1959).
(15) Schmidt, J.J.E., Krimmel, J.A., others, *Ibid.*, **56-202** Part 1-3 (1956-1958).
(16) Schmidt, J.J.E., Krimmel, J.A., Farrell, Jr., T.J., *J. Org. Chem.* **25**, 252 (1960).
(17) Smith, Alexander, Menzies, A.W.C., *J. Am. Chem. Soc.* **32**, 1412 (1910).
(18) Tolbert, B.M., Lemmon, R.M., *Nucleonics* **3**, 52-67 (1955).
(19) Wagner, R.M., Towle, L.H., WADC Tech. Rept. **58-206**, ASTIA No. **202499** (1958).

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