Physical Properties of Diarylalkanes

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Physical properties of the following compounds have been measured: 1-m-tolyl-1-p-tolylethane; 1,1-di-m-tolylethane; 1-o-tolyl-1-p-tolylethane; 1-m-tolyl-1-o-tolylethane; 1,1-di-o-tolylethane; 2,2-di-p-tolylbutane; 2-o-tolyl-2-p-tolylbutane; 1-p-propylphenyl-1-p-tolylethane; 2-p-propylphenyl-2-p-tolylbutane; 1,1-di-p-tolylethylene. For each of the compounds listed, some of the following properties are reported; the melting point, T_f, the calculated freezing point, T_o, the cryoscopic constant, K, mole per cent purity, vapor pressure, density, viscosity, refractive index, and surface tension. The heat of fusion can be calculated from T_o and K. In addition to the tabulation of the physical properties, a correlation has been shown between the structures of the ditolylethanes and their properties. The density, viscosity, refractive index, and surface tension increase continuously as the methyl groups on the phenyl rings move in from the para positions to the ortho positions.

IN CONNECTION with a program to develop a dibasic acid ester, a number of diarylalkanes were extensively characterized as to physical properties. The compounds studied included ditolyethanes, ditolylbutanes and their derivatives. The two tolyl groups were always attached to the same carbon of the alkane, and the isomers varied in the position of the methyl groups on the rings. In this series, we have correlated molecular structure and properties for the case in which the number of methyl groups remains constant and the positions vary.

SYNTHESIS

Table I lists the compounds which were studied in this work. The ethanes (with the exception of the p,p'-isomer) were prepared from the corresponding 1,1-diarylethanols via the ethylenes. The unsymmetrical ethanols were prepared by the interaction of an alkylacetophenone with the Grignard of a tolylbromide, while the symmetrical ethanols were prepared by the reaction of the appropriate tolyl Grignard with ethyl acetate. The p,p'-ditolylethane was prepared from a purified sample of the corresponding ethylene. The ethylene was synthesized by dehydrogenation of the ditolylethane mixture obtained from the alkylation of toluene with acetaldehyde. The diarylbutanes were synthesized by the sodium-catalyzed alkylation of the corresponding diarylethanes with ethylene.

PHYSICAL PROPERTIES

The physical properties measured were purity, melting point, vapor pressure, viscosity, density, refractive index and surface tension.

Determination of Purity by Cryoscopy. The initial samples of diarylalkanes were crystallized with some difficulty by one of several methods: seeding with a similar substance, thermal shock, long exposure to dry ice temperature, etc.

Table I. C.A. Nomenclature and Structure

Compound	Structure	Abbreviation
1,1-Di-p-tolylethane		pp' DTE
1-m-Tolyl-1-p-tolylethane		mp' DTE
1,1-Di-m-tolylethane		mm' DTE
1-o-Tolyl-1-p-tolylethane		op' DTE
1-m-Tolyl-1-o-tolylethane		om' DTE
1,1-Di-o-tolylethane		oo' DTE
2,2-Di-p-tolylbutane		2,2,pp' DTB
2-o-Tolyl-2-p-tolylbutane		2,2,op' DTB
1-p-Propylphenyl-1-p-tolylethane		pp' PPTE
2-p-Propylphenyl-2-p-tolylbutane		2,2,pp' PPTB
1,1-Di-p-tolylethylene		pp' DTEE

When crystalline samples of each compound had been prepared and saved, it was relatively easy to achieve crystallization of subsequent samples using the seeding technique. The freezing or melting curve of each sample was determined on the constant temperature differential cryoscopic apparatus (12). The platinum resistance thermometer was checked for accuracy at the ice point and at the benzoic acid point several times during the series. Temperatures were measured to an accuracy of $\pm 0.02°$ C.

The time-temperature cooling (or warming) curves obtained automatically on the recorder were analyzed by the Taylor and Rossini method (9). These analyses give T_f (the temperature of initial freezing) and T_o (the freezing point of pure meterial). The results obtained by this method were compared with those obtained by the $T_{1 2}$ method proposed by Witschonke (12). In most cases the agreement was quite satisfactory and within the limitations of the two methods. The cryoscopic constant, K, of om'-DTE was determined by adding several increments of benzene and measuring the freezing point depression each time. In addition K was determined for pp'-DTE from a plot of mole per cent pp'-DTE vs. temperature of melting (1). The values were in satisfactory agreement with the value computed from the equation $K = 100\ L_f/R\ T_o^2$ where L_f equals the heat of fusion. The heat of fusion was estimated from Walden's Rule which states that the entropy of fusion, L_f/T_o, is approximately equal to 13. From the values of T_f, T_o, and K the purity of each compound was calculated. This information is shown in Table II.

Two polymorphs of 1,1-di-p-tolylethane were found, one melting at $-17.78°$ and the other at $+3.13°$ C.

Vapor Pressure. The vapor pressures of pp'-DTE and op'-DTE, of pp'-DTB and op'-DTB and of pp'-PPTE were determined in this laboratory. An isoteniscope (2, 8, 10) with mercury in the differential thermometer has been utilized for measuring vapor pressures at temperatures up to $\sim 220°$ C. Table III lists the Antoine Equation constants

determined by the method of least squares. The last column of Table III gives the boiling point at 760 mm. pressure for each compound. These temperatures were determined by extrapolating the Antoine Equations to 760 mm. The temperatures have an estimated accuracy of $\pm 4°$ C., because of the large extrapolation beyond the experimental data. These compounds have a wide liquid range of the order of 300° C. This range could be extended by compounding binary or ternary systems which would lower the freezing point without affecting the boiling point appreciably. These compounds may find use as heat exchange media.

Density. The densities of the compounds from 0 to 150° C. were determined by weighing a semimicropycnometer. Distilled water was used to calibrate the pycnometer at 0° and 50° C. and mercury was used at 150° C. The samples of diarylalkanes were outgassed under vacuum at 50° C. for 1 minute to remove dissolved gases prior to the 0° C. measurements. The temperature of the thermostat was maintained to $\pm 0.2°$ C. The thermostat thermometer was calibrated against standard Anschutz thermometers. The determination of density was made in duplicate for most of the compounds.

Table IV shows the density data. The probable error of the density measurement is 0.06% at 0° and 50° C. and 0.1% at the higher temperatures. The data were extrapolated to 200° C. The density is a linear function of temperature over the range measured. Table IV shows a progressive increase in density as the structure of the ditolylethane becomes more compact—i.e., as the methyl groups on the rings move in from the para positions to the ortho positions.

Viscosity. The relative viscosities of the compounds were determined by the rate of flow through a capillary. An Ostwald viscometer was cleaned and dried for each sample and placed in a thermostatted bath. A 6-ml. sample was used in each case. The time of flow in the viscometer was measured with a stop watch to 0.1 second. Three to six determinations of the time of flow of each sample were made. Distilled water was used as the viscosity standard at 0°, a standard sucrose solution at 50° and mercury at 150° C. (6). The thermostat thermometer was checked at 50° and 150° C. against standard Anschutz thermometers and suitable corrections applied.

The following equation was used to calculate the relative viscosities of the diarylalkanes by comparison with the viscosities of the known standards.

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

Table II. Cryoscopic Data on the Diarylalkanes

Compound	T_f (or T_m), ° C.	T_o, ° C.	K, Mole %/° C[a]. Calc.	Exptl.	Purity, Mole %
pp'-DTE[b]	-17.82	-17.78	2.56	...	99.88
pp'-DTE[b]	$+3.08$	$+3.13$	2.36	2.54[c]	99.88
mp'-DTE	...	(-12)[d]	(2.5)[e]	...	...
mm'-DTE	...	(-8)[d]	(2.5)[e]	...	...
op'-DTE	-3.92	-3.76	2.43	...	99.52
om'-DTE	4.15	5;4	2.33	3.5[f]	96.3
oo'-DTE	23.57	24.3	2.2	...	97.9
2,2-pp'-DTB	-0.29	-0.14	2.38	...	99.55
2,2-op'-DTB	...	...	...	...	(95)[g]

[a] Calculated from $K = (100\ L_f/RT_o^2)$, L_f is the heat of fusion estimated from Walden's Rule. [b] Two different melting forms of pp'-DTE were found. [c] Measured cryoscopically, using other isomers of DTE as added impurities. [d] Estimated values only. These compounds never crystallized. Purity not known. [e] Calculated values of K, assuming estimated T_o's were correct. [f] Measured cryoscopically, using benzene as an added impurity. [g] Estimated from purity of starting materials.

Table III. Vapor Pressure of Diarylalkanes

Antoine Equation: $\log P_{mm} = A - B/(t + C)$

Compound	A	B	C	t_{760}, ° C.
op'-DTE	7.5122	2200.3	180	295.1
pp'-DTE	7.4289	2200.3	180	303.8
2,2-op'-DTB	7.2819	2200.3	180	319.9
2,2-pp'-DTB	7.2021	2200.3	180	329.2
pp'-PPTE	7.1377	2200.3	180	336.9

Table IV. Density of Diarylalkanes

Compound	Density, Grams/Ml.			
	0.0° C.	50.0° C.	149.8° C.	200° C.
pp'-DTE	0.9888	0.9530	0.8816	0.845
mp'-DTE	0.9918	0.9562	0.8846	0.849
mm'-DTE	0.9925	0.9594	0.8831[a]	0.852
op'-DTE	1.0024	0.9652	0.8926	0.856
om'-DTE	1.0057	0.9683	0.8951	0.858
oo'-DTE	1.0126	0.9770	0.9027	0.866
2,2-pp'-DTB	0.9882	0.9538	0.8874	0.853
2,2-op'-DTB	0.9878	0.9528	0.8852	0.851
pp'-PPTE	0.9711	0.9364	0.8865	0.832
2,2-pp'-PPTB	...	0.9380	0.8681	0.834

[a] Value appears inconsistent with rest of data. Probable value is 0.888 ± 0.001.

where

η = viscosity, cp.
d = density, grams/ml.
t = time in seconds

subscripts

1 = diarylalkane
2 = standard substance

The densities used were those reported in Table IV.

Two viscometers were used, one for the 0° and 50° C. experiments and another one with a finer capillary for the 150° measurements. At 0° C., the flow times of the diarylalkanes varied from 130 to 3900 seconds. The rate of flow of the water was 20.4 seconds. At 50° C., the flow times varied from 29 to 111 seconds, the sucrose solution time was 121 seconds. At 150° C. the times varied from 204 to 282 seconds. The mercury flow time was 25.8 seconds. A check was made to establish that the flow of water through the capillary at 0° C. was laminar, not turbulent. A calculation of the Reynolds number was made and found to well under the turbulent flow value. No correction was made for the kinetic energy term in these measurements.

The probable precision of the measured value of the viscosity is ± 0.6% at 0° and 50° C. At 150° C., the probable error is somewhat greater.

Table V shows the data. The data were extrapolated to 200° C. by the method of Othmer and Conwell (7). This method consists of plotting log viscosity of the diarylalkanes against log vapor pressure of water at the same temperature. This device lessens the curvature of the data at higher temperature and increases the confidence of the extrapolation.

Refractive Index. The refractive indices of the compounds were measured with a Bausch and Lomb precision refractometer of the modified Abbé type. The sodium D line was used as the standard light source. Temperature was held at 25.00 ± 0.05° C. Scale readings on the instrument were converted to refractive indices using the tables supplied with the instrument. The results are given in Table VI.

Surface Tension. The surface tensions of three of the ditolylethanes and of 2,2,pp'-DTB were measured by the capillary rise technique from room temperature to 200° C. The following formula was used:

$$\gamma = \tfrac{1}{2}\, hdgr$$

where

γ = surface tension, dynes/cm.
h = rise of liquid in capillary tube, cm.
d = density of liquid, grams/ml.
g = acceleration due to gravity, cm.·sec.$^{-2}$ = 980.336
r = radius of capillary, cm.

Table V. Relative Viscosity of Diarylalkanes

Compound	η, Cp.			
	0.0° C.	50.0° C.	149.8° C.	200° C.
pp'-DTE	11.63	2.53	0.574	0.377
mp'-DTE	17.35	3.02	0.603	0.387
mm'-DTE	23.83	3.60	0.658	0.425
op'-DTE	45.14	4.14	0.684	0.434
om'-DTE	76.56[a]	5.03	0.724	0.454
oo'-DTE	343.1[a]	7.84	0.812	0.501
2,2-pp'-DTB	311.5	7.45	0.753	0.468
pp'-PPTE	19.57	3.55	0.719	0.463
2,2-pp'-PPTB	...	9.36	0.913	0.556

[a] Measurements made on supercooled liquid—i.e., below normal freezing point.

Table VI. Refractive Index and Surface Tension of Diarylalkanes

Compound	n_D^{25}	Surface Tension (30° C.), Dynes/Cm.
pp'-DTE	1.55680	34.5
mp'-DTE	1.55870	...
mm'-DTE	1.56046	...
op'-DTE	1.56322	35.5
om'-DTE	1.56621	36.1
oo'-DTE	1.56882	...
2,2-pp'-DTB	1.55533	33.6
pp'-PPTE	1.54633	...
2,2-pp'-PPTB	1.54498	...

The radius of the capillary was determined using a thread of mercury, measuring its length, and then weighing it. This determination of the radius was checked by measuring the rise of distilled water in the capillary and solving for r in the above equation using the known value of γ for water. The two values agreed within 1%. Some difficulty was experienced in getting reproducible readings when the height of liquid column was established from above and from below the equilibrium level. Repeated cleaning of the capillary with hot chromic acid, hot 30% nitric acid, and distilled water resulted in satisfactory reproducibility. Figure 1 shows the results. The results are also tabulated in Table VI for 30° C. only.

Coops, Hoijtink, and Kramer (3) synthesized p,p'-DTE and o,o'-DTE and measured refractive indices of these compounds at 20° C. These values agree very closely (within 0.07%) with the values given in this report when the present values are corrected for temperature. However, Coops was not able to crystallize his compounds nor to estimate their purities.

Miscellaneous: 1,1-di-p-tolylethylene. A sample of pp'-DTEE was examined for purity by cryoscopy. The results are: T_f = 59.87° C.; T_o ' 60.04°; and purity = 99.65 mole %. No other measurements were made on this compound.

Coops, et al. (4) synthesized 1,1-di-p-tolylethylene and obtained a melting point of 60.0° C. and a melting range of 0.20° C. The present work confirms the validity of this result.

RESULTS AND DISCUSSION

The results of the measurements are given in Tables II to VI. Various physical properties measured will be functions of the purity of each compound, as well as of
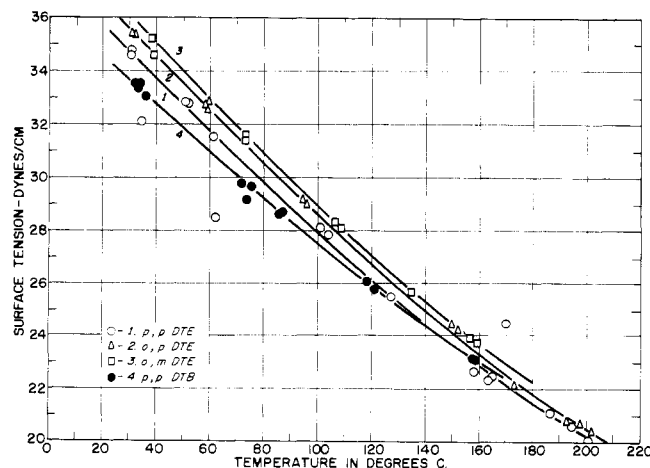

Figure 1. Surface tension vs. temperature for diarylalkanes

the structure. The purity of each compound determined from its freezing or melting point should be considered when a critical examination of the values of other properties is being made.

The increasing demands on lubricating and hydraulic fluids have promoted considerable research into the physical and chemical properties of a wide variety of substances including petroleum fractions, siloxanes, glycol ethers, phosphorus compounds, etc. Recently Wilgus, Ettling, and Pino (11) reported the results of studies of the physical properties and thermal and radiation stability of a number of diarylalkanes for use as hydraulic fluid base stocks. The conclusions were that α,ω-diphenylalkanes were very promising for this use, having good physical properties and good oxidation, heat and radiation resistance.

Dixon and Clark (5) reported correlation of the physical properties of high molecular weight alkylbenzenes and alkylcyclohexanes with their structure and showed that methyl groups attached to the benzene ring increased the density and viscosity of the compound. The fusing of rings causes the same effects. The interpretation proposed is that the rigidity of a molecule is increased by the fusing the most compact structure—i.e., the methyl groups are in as close to the ethane chain as possible—has the highest values. In addition it was not known a priori whether mm'-DTE or op'-DTE would be the denser, optically or by weight, but the measurements difinitely establish that op'-DTE is the more dense. Figure 2 shows the variation of the physical properties on an arbitrary scale, which, however, is proportional to the true values for each property.

CONCLUSION

For the physical properties of the six isomers—density, refractive index, surface tension, and viscosity—there is a continuous change as a function of the structure. The order of the properties is as follows: $pp' < mp' < mm' < op' < om' < oo'$. The least compact structure, pp'-DTE, has the lowest values of these properties, and oo'-DTE, of rings or by the addition of methyl groups to a phenyl ring. They suggested that hyperconjugation of the methyl groups attached to the ring created a significant double bond character in the C—C bond between the ring and methyl group and raised the barrier to wagging of the methyl group. Hydrogenation of the ring eliminated this hyperconjugation, and the anomalous density, viscosity and molecular attraction disappeared. Steric hindrance of the substituents did not seem to be the cause of the anomalous properties in their series.

From this regularity of properties for the DTE series, it is not to be inferred that the same conclusion can be drawn regarding the DTB series. The pp'-DTB is the only known-purity sample of the series available. The properties of the op'-DTB were measured, but its purity could not be determined by cryoscopy. As shown by NMR, the op'-DTB was a mixture of several products.

More work on the DTB series remains to be done when the compounds become available. The regularity in the properties of DTE as a function of structure was not established for the DTB series due to the limited data.
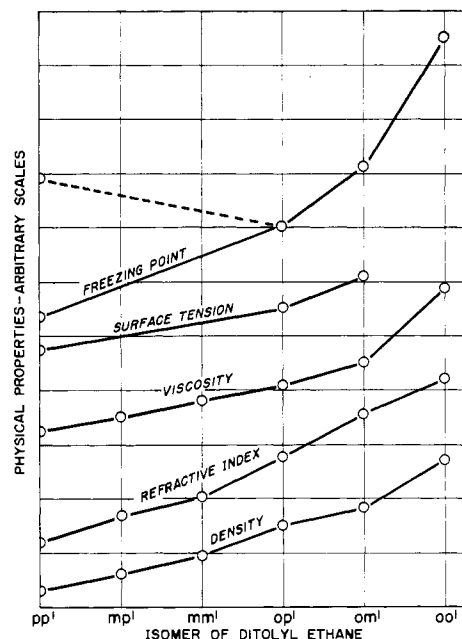

Figure 2. Physical properties of the ditolyl-ethanes as function of structure

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