Physical Properties of High Molecular Weight Alkylbenzenes and Alkylcyclohexanes

JOSEPH A. DIXON and SIDNEY G. CLARK, II[1]
The Pennsylvania State University, University Park, Pa.

As a portion of its continuing study of hydrocarbon properties and molecular structure American Petroleum Institute Research Project 42 has synthesized and determined the physical properties of more than 80 alkylbenzenes and alkylcyclohexanes (*10*). Most recently four polyalkylbenzenes and polyalkylcyclohexanes of a structural type not previously studied have been synthesized (*1*). These new monocyclic hydrocarbons which possess one long normal-alkyl substituent and two or three methyl substituents are of a molecular type recently proposed as being prominent in the lubricating oil fraction of petroleum (*4*). Comparison of their physical properties with properties of other alkylbenzenes and alkylcyclohexanes of the same molecular weight reveals some interesting structure-property relationships.

PROPERTIES

In Table I are collected physical property data for five representative high-mass alkylbenzenes previously prepared at Penn State and the two polymethyl substituted benzenes recently completed. In Table II are the data for the corresponding cyclohexane derivatives. This discussion is confined to those structure-property effects wherein the polymethylbenzenes appear to behave significantly differently from other alkylbenzenes. Schiessler and others (9) have given excellent discussions of the latter. Considering first the aromatic hydrocarbons, it may be seen that branching of the long normal alkyl chain (PSU 82 and 161, Table I) or conversion of the chain into two shorter alkyl groups (PSU 152 and 208) results in a small increase in molar volume (slightly decreased density). A different type of branching—replacement of chain methylenes by methyl branches on the ring—produces a significant decrease in molar volume (increased density).

American Petroleum Institute Research Project 42 has shown that the Kurtz-Lipkin equation (*6*) for calculating molar volume, which is excellent for most hydrocarbon types, consistently yields low values for most higher molecular weight alkylbenzenes (*10*). In contrast this relation predicts the molar volume of PSU 158 almost exactly and gives a value 7.6 ml. too large for the mesitylene derivative(PSU 156).

The viscosity of the xylene derivative, 2,5-dimethyloctadecylbenzene, is approximately 20% larger than the viscosity of 1-phenyleicosane (PSU 99) or 1,4-didecylbenzene (PSU 152). The viscosity of the mesitylene derivative is almost 100% larger. To make the comparisons free of molecular weight differences, the properties of 2,4,6-trimethylheptadecylbenzene, a C_{26}, were calculated from the values for the corresponding C_{27} (PSU 156).

Probably the most striking differences in the behavior of these polymethyl aromatic hydrocarbons are observed on hydrogenation of the aromatic ring (Table III). The viscosity data for the first four structures in Table III are in accord with the well-known generalization that hydrogenation of alkyl benzenes results in a significant increase in viscosity (*5*). However, the benzenes with one or two methyl groups on the ring exhibit only a very slight increase or decrease in viscosity on hydrogenation and the trimethyl derivative undergoes a 30% decrease in viscosity when hydrogenated.

DISCUSSION

It is interesting to consider how these physical property effects may arise from the structural changes in the molecules. Although each of the polymethylbenzenes discussed here has at least one methyl group ortho to the long alkyl chain, steric interference of these substituents does not appear to be the principal cause of the "anomalous" properties. From a study of molecular models it appears that the interference of the methyls with the long alkyl group in the perhydro derivatives should be similar to that in the aromatic hydrocarbons, but the polymethylcyclohexanes show no anomalous physical properties (Table II). Indeed, the physical properties of 1-cyclohexyleicosane and 2,4,6-trimethyl-*n*-heptadecylcyclohexane are strikingly similar.

A possible explanation of the viscosity increase and the density increase which accompany the substitution of methyl groups on the benzene nucleus might be as follows. Because of a resonance effect—e.g., hyperconjugation (*12*)—the carbon-carbon bond between the aromatic ring and the methyl group probably has a significant amount of double bond character. The barrier to "wagging" about such a bond might be significantly higher than about a normal carbon-carbon single bond and it has been observed that restricted intramolecular motion in a molecule results in increased viscosity (*2*). Previous comparisons (*10*) of the densities of fused-ring and non-fused-ring polycyclic aromatic hydrocarbons having the same molecular weight and the same number of carbon atoms in rings led to the conclusion that increasing the rigidity of the hydrocarbon molecule results in a higher density (lower molecular volume). Thus, if in the present case a resonance effect tends to restrict the out-of-plane motion of the methyl groups on the aromatic ring, the over-all rigidity of the molecule is increased and the increased density then follows logically. Further indirect support for this explanation of the anomalous properties is obtained if one considers 2,4,6-trimethyloctadecylbenzene to have 9/27 rather than 6/27 of its carbon atoms in rings for the physical properties of this hydrocarbon then fit the qualitative correlations of viscosity and density with "per cent carbon atoms in rings" suggested some years ago by Schiessler and others (9).

An additional factor producing the increased densities, increased boiling points, and increased resistance to viscous flow of the polymethylbenzenes may be the delocalization of the methyl group electrons (due to hyperconjugation) resulting in increased intermolecular interaction of the phenyl ring pi electrons and thus increased intermolecular attraction.

Schiessler and others observed that when alkyl-substituted, fused-ring aromatics are hydrogenated, the viscosity decreases while the kinetic viscosity index and viscosity-temperature rating (*7*) increase (Table IV). This is exactly opposite to the behavior of the noncondensed ring aromatics previously prepared by the Penn State Hydrocarbon Laboratory but entirely analogous to the behavior of these new polymethyl derivatives. These methyl groups act as members of a rigid "pseudo-fused-ring" aromatic system and when, upon hydrogenation, the rigidity and planarity of the ring system are lost the additional barrier to motion disappears. It thus appears that these data in Tables I, II, and III may be rationalized on the basis that

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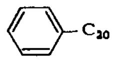
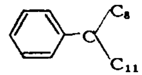
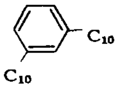
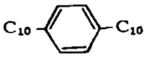
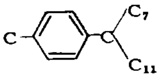
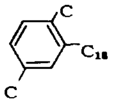
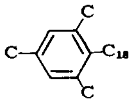
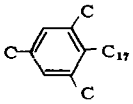
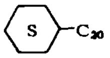
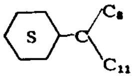
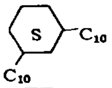
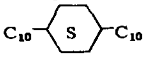
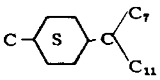
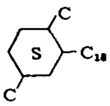
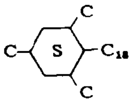
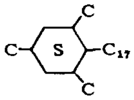
[1] Present address, Monsanto Chemical Co., St. Louis, Mo.

Table I. Physical Properties of Some High Molecular Weight Alkybenzenes

PSU No.	Structure[a]	Viscosity, Cs., 37.8°C.	KVI	VTR[b]	Density, G./Ml., 37.8°C.	Molar Volume[c] Found	Molar Volume[c] Calcd.[d]	Refractive Index, 20°C.
99[e]		11.5	160	−1.127	0.8430	419.8	417.1	1.4801
82[e]		13.86	126	−1.335	0.8424	420.4	417.1	1.4790
208[e]		11.45	151	−1.184	0.8411	420.6	417.1	1.4813
152[e]		12.14	154	−1.174	0.8414	420.4	417.1	1.4821
161[e]		16.28	112	−1.426	0.8413	420.4	417.1	1.4808
158		14.59	135	−1.322	0.8473	417.4	417.1	Solid
156		22.50	121	−1.486	0.8513	425.7	433.3	Solid
...[f]		20.4	120	−1.464	0.8513	...	...	...

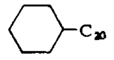
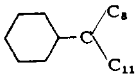
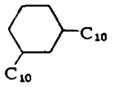
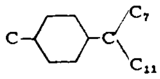
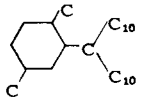
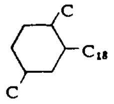
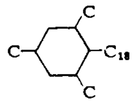
[a] C_n refers to a straight chain of n-carbon atoms.
[b] VTR viscosity temperature rating is average percentage decrease in viscosity between 100 and 210°F. (7).
[c] In ml. per mole at 20°C.
[d] (6).
[e] (10).
[f] Properties shown are calculated values.

Table II. Physical Properties of Some High Molecular Weight Alkylcyclohexanes[a]

PSU No.	Structure	Viscosity, Cs., 37.8°C.	KVI	VTR	Density, G./Ml., 37.8°C.	Molar Volume Found	Molar Volume Calcd.	Refractive Index, 20°C.
100		16.4	150	−1.259	0.8208	438.3	435.7	1.4623
78		16.14	122	−1.387	0.8256	435.8	435.7	1.4635
209		14.95	143	−1.279	0.8202	438.5	435.7	1.4618
153		16.55	148	−1.274	0.8217	437.7	435.7	Solid
162		17.52	113	−1.444	0.8241	436.5	435.7	1.4630
159		15.39	145	−1.275	0.8212	438.1	435.7	1.4619
157		17.60	144	−1.311	0.8232	453.9	452.0	1.4629
...		15.48	142	−1.296	0.8228	437.4	435.7	...

[a] See footnotes Table I.

Table III. Effect of Hydrogenation on Viscosity and Viscosity Index of Alkylbenzenes[a]

Structure[b]	% Change[c] in Viscosity at 37.8° C.	ΔKVI[d]	VTR$_{al}$/VTR$_{ar}$[e]
	43.	−10	1.12
	16.	−4	1.04
	31.	−8	1.08
	7.6	+1	1.01
	−1.3	+38	0.99
	5.5	+10	0.96
	−22.	+23	0.88

[a] (*10*).

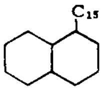
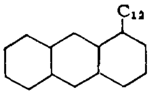
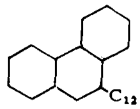
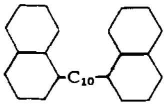
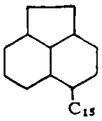
[b] C_n refers to a straight chain of *n* carbon atoms.

[c] $\frac{Z_{cs.}(\text{alicyclic}) - Z_{cs.}(\text{aromatic})}{Z_{cs.}(\text{aromatic})} \times 100.$

[d] Kinematic viscosity index of alicyclic hydrocarbon minus KVI of aromatic.

[e] Ratio of VTR of alicyclic hydrocarbon to VTR of corresponding benzene. See (*7*) for definition of VTR.

Table IV. Effect of Hydrogenation on Viscosity and Viscosity Index of Some Fused Ring Aromatic Hydrocarbons[a]

Structure	% Change in Viscosity at 37.8° C.	ΔKVI	VTR$_{al}$/VTR$_{ar}$
	3.5	14	0.96
	−40.	48	0.85
	−24.	30	0.91
	−29.	69	0.86
	−15	22	0.91

[a] Reference (*10*).

hyperconjugation of the methyl group with the aromatic ring results in restriction of the out-of-plane motion of the methyl groups and increased intermolecular attraction.

Hastings and Nicholson (*3*) calculated on the basis of vibrational assignments and the entropy data, the rotational barriers for the ortho and central methyl groups in 1,2,4- and 1,2,3-trimethylbenzene. These are 1400 and 3200 cal. per mole, respectively, as compared to 3400 cal. per mole for ethane (*11*). Thus restricted rotation in these systems does not appear to make a significant contribution to the observed anomalous physical property effects.

COMPOSITION OF LUBRICATING OIL

Upon hydrogenation of the lubricating oil fraction from petroleum the viscosity drops markedly and the viscosity index increases. These facts, in conjunction with the pure hydrocarbon data, have been cited (*5,8*) as evidence that the aromatic hydrocarbons in the lubricating oil fraction are predominantly of the fused ring type. It appears from the data in Table III, however, that the results obtained in hydrogenating oil fractions cannot be used to exclude the possibility of significant amounts of nonfused polymethylbenzenes being present in these materials. Most recently Hood, Clerc, and O'Neal proposed (*4*) on the basis of mass spectra that the alkyl substituents of the typical benzene hydrocarbon in lubricating oil must consist of one long chain alkyl group and one or more methyl or ethyl groups. The physical property data reported here appear to be entirely consistent with their picture of the nonfused aromatic structures present in this petroleum fraction.

ACKNOWLEDGMENT

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