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Abstract

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On the Question of a Spectral Method for Determining the Number and Position of Side Chains in Molecules of Benzene Homologs

(Presented by Academician B. A. Kazanskii, May 24, 1957)

In a previous communication (^1) we showed that the ultraviolet absorption spectra of crystals of benzene homologs, obtained at the temperature of liquid nitrogen (77°K), can be used for rapid determination of the number and position of side chains in these hydrocarbons. The quantity of substance required for this is very small, amounting to several hundredths of a gram. Absorption spectra at the temperature of liquid nitrogen consist of series of narrow bands, of the same type for compounds with the same arrangement of side chains, independently of their size and branching.

If photographs of the spectra of compounds with the same type of substitution in the molecules are superposed so that the first absorption bands, corresponding to the purely electronic transition, coincide, then all subsequent bands also coincide. In this case the relative intensities of the bands are also reproduced. Such a superposition cannot be made for compounds with different types of substitution in the molecules.

This was demonstrated (^1) on a large number of examples for a series of monoalkylbenzenes, and also for some of the simplest representatives of *o*- and *n*-dialkylbenzenes.

In the present communication we give further data confirming the indicated regularities.

The physical properties of the hydrocarbons studied are given in Table 1.

Using the examples of 1,2,4-trialkylbenzenes (Fig. 1A) and 1,2,3,5-tetraalkylbenzenes (Fig. 1B), it is shown that in these series as well the uniformity of the spectra is preserved as the length of the side chain increases. Further, the similarity of the spectra of *n*-diisopropylbenzene and *n*-xylene confirms that the branching of both side chains is not reflected in the positions of the absorption bands (Fig. 1B).

Of special interest is the fact that the absorption spectra of hydrocarbons with the same arrangement of side chains retain similarity to one another even when a double bond, not conjugated with the benzene nucleus, is introduced into the side chain, as is evident from comparison of the spectra of ethyl- and propylmesitylene with allylmesitylene (Fig. 1B) and of toluene with 2-methyl-3-phenylpropene-1 (Fig. 1G). A completely different picture is observed when the double bond is directly conjugated with the benzene nucleus. Thus, the absorption spectrum of 2-methyl-1-phenylpropene-1 proves to be continuous even at the temperature of liquid nitrogen; the absorption intensity in it is considerably greater than in the other compounds studied.

Table 1

Physical properties of the hydrocarbons studied

Hydrocarbon	Structure	B.p., °C/mm Hg	Freezing point, °C	n_D^{20}	d_4^{20}	Degree of purity, %
Pseudocumene	benzene ring with CH_3 groups in the 1,2,4-positions	79.8-79.9/38.5	–	1.5050	0.8757	not determined
Ethyl-*p*-xylene	benzene ring with CH_3 groups in the 1,4-positions and C_2H_5 in the 2-position	104.5/57	–	1.5043	0.8772	not determined

Hydrocarbon	Structure	B.p., °C/mm Hg	Freezing point, °C	n_D^{20}	d_4^{20}	Degree of purity, %
Ethylmesitylene	benzene ring with CH_3 groups in the 1,3,5-positions and C_2H_5 in the 2-position	99.3/20	−12.1	1.5103	0.8859	99.7
n-Propylmesitylene	benzene ring with CH_3 groups in the 1,3,5-positions and CH_2—CH_2—CH_3 in the 2-position	100.2/11.7	−20.5	1.5052	0.8782	99.7
Allylmesitylene	benzene ring with CH_3 groups in the 1,3,5-positions and CH_2—CH=CH_2 in the 2-position	105.5/16	−2.1	1.5194	0.8989	98.9

Figure 1

Figure 1: Figure 1

Hydrocarbon	Structure	B.p., °C/mm Hg	Freezing point, °C	n_D^{20}	d_4^{20}	Degree of purity, %
p-Diisopropylbenzene	benzene ring with two $CH_3—CH—CH_3$ groups in the para positions	95.5/18.5	−17.1	1.4900	0.85679	99.5
2-Methyl-3-phenylpropene-1	$C_6H_5—CH_2—C(CH_3)=CH_2$	76.8/27	—	1.5081	0.8825	not determined
2-Methyl-1-phenylpropene-1	$C_6H_5—CH=C(CH_3)—CH_3$	87.9/27	—	1.5399	0.9022	not determined

It is necessary to note the substantial difference in the construction of the spectra of alkyl- and alkenylmesitylenes (Fig. 1B) and monoalkylbenzenes (Fig. 1G), which makes it possible to identify these molecules spectrally, despite the fact that their symmetry is the same (there is a symmetry axis of the second order and two mutually perpendicular planes of symmetry).

Table 2 gives the frequencies of the bands of purely electronic transitions in the spectra of the compounds studied.

All hydrocarbons used for the investigations were prepared by methods ensuring that they were obtained in a very pure state. Determination of the degree of purity of some of them ([2,3]) on the basis of freezing curves and cryoscopic constants fully confirmed this.

For the article by O. V. Bragin, V. L. Broude, S. V. Zotov, A. L. Liberman, O. S. Pakhomova, and M. A. Pryanishnikov, p. 961

Fig. 1. Absorption spectra of crystals at a temperature of 77° K: 1 —pseu-

Figure 1

Figure 2: Figure 1

documene, 2 —ethyl-*n*-xylene, 3 —ethylmesitylene, 4 —*n*-propylmesitylene, 5 —allylmesitylene, 6 —*n*-xylene, 7 —*n*-diisopropylbenzene, 8 —toluene, 9 —2-methyl-3-phenylpropene-1

For the article by K. I. Portnoi and G. V. Samsonov, p. 976

Fig. 1. Microstructures of alloys $(Ti, Cr)B_2$—ZrB_2 (500×).
a —100% $(Ti, Cr)B_2$; *b* —100% ZrB_2;
c —$(Ti, Cr)B_2 + 10\%ZrB_2$; *d* —$(Ti, Cr)B_2 + 60\%ZrB_2$

Table 2

Frequency of purely electronic transitions in the spectra at —190°C

No.	Hydrocarbon	State of the sample	Frequency, cm^{-1}
1	Pseudocumene	Crystal of the low-temperature modification	36330
2	Ethyl-*p*-xylene	Polycrystal of the low-temperature modification	36360
3	Ethylmesitylene	Crystal of the low-temperature modification	36000
4	*n*-Propylmesitylene	Polycrystal of the high-temperature modification	36020
5	Allylmesitylene	Polycrystal	36200
6	*p*-Diisopropylbenzene	Crystal	36900
7	2-Methyl-3-phenylpropene-1	Crystal	37140

Experimental Part

Pseudocumene. Obtained by diene condensation of acrolein with isoprene to give 1,3-dimethyl-4-formylcyclohexene-1, which was then converted by the

Kizhner hydrazone method into 1,3,4-trimethylcyclohexene-1. Dehydrogenation of the latter over platinized charcoal gave pseudocumene, which was chromatographed on silica gel and distilled on a column with an efficiency of 40 theoretical plates.

Ethyl-*p*-xylene. Obtained from very pure *p*-xylene, prepared by repeated freezing out and crystallization of a commercial product. By bromination it was converted into 2-bromo-*p*-xylene, and then, by the reaction of magnesium bromo-*p*-xylene with diethyl sulfate, ethyl-*p*-xylene was obtained. The latter was chromatographed on silica gel, distilled on a column of 40 theoretical plates, and again chromatographed.

Ethylmesitylene. Obtained from synthetic mesitylene, carefully purified by distillation and chromatography, by converting it into bromomesitylene and then treating magnesium bromomesitylene with diethyl sulfate. Ethylmesitylene was purified by recrystallization from ether at −60°C, chromatography on silica gel, fractionation on a column with an efficiency of 50 theoretical plates, and repeated recrystallization.

***n*-Propylmesitylene.** Obtained in the same way, but instead of diethyl sulfate the *n*-propyl ester of *p*-toluenesulfonic acid was used. *n*-Propylmesitylene was purified by distillation on a column with an efficiency of 50 theoretical plates.

***p*-Diisopropylbenzene.** Isolated from technical diisopropylbenzene by converting the isomeric diisopropylbenzenes into sulfonic acids and hydrolyzing the latter with steam at a temperature of 100°C; under these conditions chiefly *p*-diisopropylbenzenesulfonic acid undergoes hydrolysis. *p*-Diisopropylbenzene was purified by crystallization from ether at a temperature of −60°C, and then by distillation on a column with an efficiency of 80 theoretical plates.

2-Methyl-3-phenylpropene-1 and 2-methyl-1-phenylpropene-1. Obtained from benzylmagnesium chloride and acetone via dimethylbenzylcarbinol. From the latter, by dehydration under the action of several drops of sulfuric acid, a mixture of both methylphenylpropenes was obtained, which was then separated by fractionation on a column with an efficiency of 80 theoretical plates.

Allylmesitylene. Obtained in the same way as ethylmesitylene, but allyl chloride was used instead of diethyl sulfate. Allylmesitylene was purified by distillation on a column with an efficiency of 50 theoretical plates and by recrystallization from ether.

It should be noted that all fractionations of hydrocarbons on columns were carried out in vacuum at the pressures indicated in Table 1.

The results presented from the study of the spectra of seven hydrocarbons confirm the earlier conclusions concerning the possibility of determining, by the spectral method, the number and positions of side chains in benzene homologues, and also make it possible to extend this method to tri- and tetraalkylbenzenes.

We take this opportunity to express our sincere gratitude to Corresponding Member of the Academy of Sciences of the Ukrainian SSR A. F. Prikhot' ko and Academician B. A. Kazanskii for their constant interest in the work being carried out.

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Note: Figure translations are in progress. See original paper for figures.