ucts were recovered by extraction with boiling carbon disulfide in the presence of water. After drying with calcium chloride the extract was submitted to gas–liquid chromatographic and infrared analysis. The infrared analysis was carried out using the following bands.

ortho-Fluorobiphenyl	1110 cm.$^{-1}$
meta-Fluorobiphenyl	879 cm.$^{-1}$
para-Fluorobiphenyl	837 cm.$^{-1}$
Biphenyl	737 cm.$^{-1}$

The accuracy of the infrared analyses based on mixtures of known composition is within ±3 relative %. The gas–liquid chromatographic analysis has been reported previously.[7]

Separation of the *ortho* isomer from the *meta–para* isomer was good, that of *meta* from *para* reasonable with a higher error of determination when the *meta* isomer was present only in small amounts. Separation of *para* and *meta* isomers on more loosely packed columns than those used in previous work[7] gave shorter retention times and poorer separation. It was possible to obtain partial separation of *meta–para* isomers by lowering the column temperature to 160° with retention times of *meta* isomer of 55.6 and *para* isomer of 56.5 min. (Previous retention times at 190° were 38 and 40 min. on the tightly packed columns used, but only 18 min. under the same conditions, without separation, on presently used looser column.) As these conditions were unsatisfactory, isomer mixtures were analyzed by combining gas chromatography and infrared analyses. The *ortho* isomer was well separable from the combined *para–meta* isomers by gas chromatography and the *para* and *meta* isomers could be determined by infrared analysis. Golay columns (polypropylene glycol) were tried and found unsuitable for the *para–meta* separation.

The normalized per cent isomers in Table I are believed to be correct to within ±1 unit, based on treatment and analysis of mixtures of known composition.

Acknowledgment.—We thank Dr. D. S. Erley of the Chemical Physics Research Laboratory, The Dow Chemical Co., Midland, Michigan, for carrying out the infrared analyses.

(7) G. A. Olah and W. S. Tolgyesi, *J. Org. Chem.*, **26**, 2053 (1961).

Molecular Weight Determination by N.m.r. Spectroscopy

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Received December 12, 1962

In contrast to other types of spectroscopy used in organic chemistry, nuclear magnetic resonance spectroscopy can be used for quantitative analytical measurements without the knowledge of extinction coefficients, since such a coefficient is constant and independent of the chemical environment of the nuclei under inspection. This makes n.m.r. spectroscopy a very powerful quantitative tool. So far, its application[1] includes the measurement of extent of isotope substitution, the analysis of mixtures, per cents of hydrogen, proton counting, and interpretation of spectra in general, where integration is combined with chemical shift and splittings measurements.

We propose to apply n.m.r. integration for the determination of molecular weights. The method consists of comparing the integrated intensities of an added standard and a recognizable peak or group of peaks of the unknown in a solution containing a known weight of standard and unknown. The molecular weight is then given by the following formula.

$$M = \frac{I_s\, n\, W\, M_s}{I\, n_s\, W_s}$$

M = the molecular weight of the unknown
I_s = the intensity of the standard
I = the intensity of the unknown
n = the number of protons in the recognizable peak or group of peaks of the unknown
n_s = the number of protons of the standard peak
W = the weight of the unknown
W_s = the weight of standard
M_s = the molecular weight of standard

The method can be combined with taking the n.m.r. spectrum of the unknown; the only extra work required is the weighing of sample and standard, and the calculation. The values are not affected by dissociation and solvent interaction phenomena or various other effects that cause great errors in methods dependent on ideality in colligative properties of liquids. The error resulting from impurities is proportional to their weight and not to the molar amount. On the assumption that most impurities are smaller molecules than the unknown, this method gives smaller errors than the cryoscopic, etc., methods. The standard also serves as a marker for chemical shift calibration. Hopefully, in the future n.m.r. tubes and spectrometers can be standardized, stabilized, and precalibrated well enough, so that precise integrations can be performed without the use of a standard, similarly to our present-day ultraviolet intensity measurements.

On the other hand the method requires that at least one peak or group of peaks of the unknown be recognized as to the number of protons it contains; this absorption should not overlap with others, since otherwise the integration is very subjective. Molecules related as monomers and symmetrical dimers cannot easily be distinguished by the n.m.r. method, since they show very similar spectra. In some other cases too, difficulties arise in assigning a chosen absorption the number of hydrogens it represents. In general, however, one knows which hydrogens of a known starting material should end up unchanged in an unknown product under given reaction conditions, and use those for the determination. The choice can best be made once the n.m.r. spectrum is taken and perhaps integrated.

Experimental

The Standard.—Based on our experience the most suitable standard is hexamethyl cyclotrisiloxane, m.p. 64.5°, b.p. 133°, a very soluble inert solid, which can be removed by sublimation. There is no loss by sublimation if it is weighed last and dissolved and stoppered immediately. Its absorption at 9 c.p.s. is conveniently outside other absorptions. Any other (preferably) single peak pure material can be used as standard if its absorption can be separately seen in the spectrum. All these standards mark the chemical shift scale at the same time, and no tetramethylsilane is needed. Other possible standards include: iodoform at 294, benzoquinone at 406, *p*-dinitrobenzene at 507, and 1,3,5-trinitrobenzene at 566 c.p.s. The nitroaromatic standards should be used with caution, since occasional complex formation with aromatic unknowns offsets the results.

Procedure.—The unknown and standard should be weighed into the n.m.r. tube to give about equal intensities, completely homogenized with solvent, the spectrum taken, integrated, the chosen absorption and standard individually integrated accurately, utilizing the full chart range for the bigger of the two,

(1) "Quantitative Measurements by High Resolution NMR," Varian Associates technical information bulletin, Vol. 3, No. 1.

TABLE I

TEST OF MOLECULAR WEIGHT DETERMINATION BY N.M.R.

Unknown	*M*, calcd.	*M*, found	Peaks used for integration
Acenaphthene	154.20	155.3[a]	C_2H_4
		148.3	
		152.9	
		152.4	Aromatic hydrogens
		150.6	
		153.6	
4-*t*-Butylcyclohexanol *cis* and *trans* mixture	156.26	150.3	*t*-Butyl group
		150.1	H–C–O–
Dehydroabietonitrile	281.42	271.3	Four methyls
		267.5	Aromatic H_3
2,4-Bispentamethylenespiro-5-carboxymethylene-1,3-dioxacyclopentane in form of methyl ester	266.33	272.4	Methyl ester
2-*p*-Anisoylpropionic acid Me ester	222.23	214.5	Lower aromatic H_2
		223.0	Higher aromatic H_2
		217.7	Aromatic methoxy
		211.0	Methyl ester
		217.3	2-Methylene
		226.0	H_{10} of Me's and C_2H_4
		221.6	Aromatic H_4
Anisaldehyde	136.14	138.7	Methoxy
		141.7	Aromatic H_4
Iodoform	393.78	392.5	Single peak
Benzoquinone	108.09	110.9	
p-Dinitrobenzene	168.11	174.1	
1,3,5-Trinitrobenzene	213.11	221.9	
Diphenylacetic acid	212.24	211.7	Tertiary H
Cholesterol	386.64	374.8[b]	Olefinic H
1,2-Diacetoxy-4-*p*-anisylbutene-3	278.29	280.1	Lower aromatic H_2
		271.0	Higher aromatic H_2, lower olefinic H
		290.8	Acetates
		288.8	
		283.6	
		270.5	Aromatic H_4, lower olefinic H
		268.0	Higher olefinic H–C–O–
		281.9	Aromatic H_4, olefinic C_2H_2, H–C–O–
p-Anisylacetic acid	166.18	163.0	Methylene, methoxy
		167.1	
		162.4	Lower aromatic H_2
p-*t*-Butylacetanilide	191.26	198.8	Acetyl
		196.8[b]	
		187.0	*t*-Butyl

[a] Different values based on the same peaks were determined using different R_f field strength and sweep time. [b] 1,3,5-Trinitrobenzene used as standard. Hexamethylcyclotrisiloxane served as standard in all other determinations.

tracing about five times in both directions. Substitute the average intensities and the weights into the formula. Note that for the purposes of the determination any solvent can be used whose absorption lies outside the standard and region of interest.

Possible Sources of Error.—Inhomogeneity might cause standard and unknown to be exposed to different field strength inside the probe. Hydroxyl groups exchange with moisture in the solvent and should not be used in the determination. Overlap of peaks can seriously reduce the accuracy of the integration. Note that if two peaks of unequal intensity and/or shape overlap, it is erroneous to cut the region by a vertical line at the lowest point of the spectrum between the peaks. Errors from impurities, inaccurate weighing or reading of the integral are self-evident.

TABLE II

EXAMPLES OF CONDITIONS FOR MEASUREMENTS ON THE VARIAN A 60 SPECTROMETER

Filt. bandwidth	1	1	1	1
R_f field	0.02	0.12	0.6	0.14
Sw. time	500	500	50	500
Sw. width	500	1000	500	1000
Sw. offset	0	0	0	0
Spect. amplitude	1.6	10	32	4
Int. amplitude	20	50	20	8
Spin	Yes	Yes	No	Yes
Standard	Sil[d]	Sil[d]	Sil[d]	Sil[d]
Mg.	110.8	11.852	51.6	35.7
Meq.	8.99	0.961	4.18	2.89
Unknown	[a]	CHI_3	[b]	[c]
Mg.	254.8	64.383	101.5	87.4
Obsd. peaks	C_2H_4	CHI_3	Arom.	Ac
Meq. peaks	6.608	0.1636	1.083	1.372
No. traces	5 + 5	1 + 1	5 + 5	1 + 1
Solvent	$CDCl_3$	$CDCl_3$	CCl_4	$CDCl_3$
Ml.	0.5	0.5	0.6	0.9

[a] Acenaphthene. [b] Dehydroabietonitrile. [c] *p*-*t*-Butylacetanilide. [d] Sil, hexamethylcyclotrisiloxane.

Procedures for precise integration are discussed in operating manuals; we mention only a few crucial points here. Saturation must be avoided. Errors from saturation are greatest if sample and unknown peak are of unequal shape or size. Fluctuations due to instability (noise) are corrected by averaging several traces. If overlap is not produced by peak broadening, the sample spinning can be stopped, much higher R_f field used without saturation, and noise greatly reduced.

Tables I and II illustrate the usefulness of the new method and give the relevant information on the conditions of some of the measurements.

Acknowledgment.—The author wishes to express his gratitude to Dr. Gerald Dudek and Professor E. J. Corey for helpful comments and discussions and to the U. S. Public Health Service for a fellowship.

Preparation and Mass Spectrum of Hexachlorocyclopropane

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Received January 17, 1962

Although hexafluorocyclopropane has been known for some time,[1] hexachlorocyclopropane has not been reported previously.[2] We have prepared this compound

(1) A. F. Benning, F. B. Downing, and J. D. Park, to Kinetic Chemicals, Inc., U. S. Patent 2,394,581 (February 12, 1946).

(2) As this communication was being prepared to go to press, an abstract by S. W. Tobey and R. C. West reported the synthesis of hexachlorocyclopropane from tetrachloroethylene, chloroform, and potassium hydroxide. Their work was presented before the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962. More recently we learned through a referee that W. R. Moore, S. E. Krikorian, and J. E. LaPrade also have prepared this compound and measured its mass spectrum.