activation energies, and the frequency factors are considerably higher for the furan compounds than for corresponding benzene derivatives.

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[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Ultrasonic Investigation of Molecular Properties of Liquids. IV. Cyclic Compounds[1]

BY ALFRED WEISSLER

Recent interest in the chemical applications of ultrasonics has prompted several studies[2-6] of the relation between sound velocity and molecular structure of liquids, mainly in the aliphatic field. An emerging conclusion is that the velocity of sound is a useful and important physical property, comparable to density or refractive index.

The present work was undertaken in order to extend the correlation between sound velocity and chemical structure into the classes of aromatic, alicyclic, and heterocyclic compounds. In order to simplify the interpretations, molecules containing a substituent instead of hydrogen on a ring carbon were excluded. For a few of the twenty-two liquids chosen, the velocity had been measured previously at scattered temperatures; these were included here because of the necessity for self-consistent data at a standard temperature.

Experimental

The compounds were obtained from commercial sources, except for 1,4-thioxane, which was synthesized[7] from β,β'-dichlorodiethyl ether and alcoholic sodium sulfide. Each was purified before use by fractional distillation through a 40-cm. Widmer column. In order to free pyrrolidine from tenaciously-held water, it was let stand over sodium for a day, then distilled from sodium.

A three-megacycle ultrasonic interferometer, designed by Mr. Burton G. Hurdle, was used to measure sound velocities. This instrument is very similar to the one-megacycle interferometer previously described,[2] but it requires only 10 ml. of sample, because of the further scaling-down of physical dimensions permitted by the higher frequency.

If desirable, one could construct an ultrasonic interferometer which requires only a few drops of liquid sample, merely by going to a somewhat higher frequency. This illustrates the decisive advantage of ultrasonic frequencies in measuring the velocity of sound.

To minimize contamination by corrosion of the brass interferometer cell, all interior surfaces were gold plated. A 0.003-inch tantalum foil was used as the floor of the cell, directly beneath which lay the quartz crystal source of ultrasound.

Refractive indices for D light were determined with an Abbe refractometer, and densities with a 25-ml. pycnometer. Measurements of all three physical properties were made at 30°.

Results and Discussion

The values of sound velocity, density and refractive index for the twenty-two compounds are listed in Table I. These velocities lie in the range 1100–1550 meters/second, just as is the case for the majority of unhalogenated liquids. The estimated accuracy for the velocities is about ±0.03%.

It is apparent from the table that a compound with two rings in the molecule possesses a higher sound velocity than that associated with either of the constituent rings. Other generalizations are difficult to find, however. For example, it is not true that a five-membered ring always has a lower (or a higher) velocity than its six-membered homolog; cyclopentane's is lower than cyclohexane's, but tetrahydrofuran's is higher than tetrahydropyran's.

The present data vitiate a conclusion drawn by Schaafs,[8] to the effect that in a pair of unhalogenated liquids of practically the same molecular weight, the one with the higher density also has the higher sound velocity. Both thiophene and dihydropyran have a molecular weight of 84.1, yet thiophene has the higher density but the lower sound velocity. Similarly, cyclopentene has a lower density than furan, but a higher velocity, although both have a molecular weight of 68.1.

Thus it appears that any correlations would have to take into account the specific force-interactions between molecules due to the chemical structure. For this purpose, the adiabatic compressibility is more suitable than the raw sound velocity.

Adiabatic Compressibility.—From the sound velocity v and density d, the adiabatic compressibility K_{ad} of a medium may be calculated readily, using the relation

$$K_{\text{ad}} = 1/v^2d \qquad (1)$$

The values so obtained, presented in Table I, support the following generalizations. Increasing the saturation of a six-membered ring, as from benzene to cyclohexane, causes the adiabatic compressibility to increase also. Even if a nitrogen or oxygen atom is substituted for one of the six carbons, as in the pyridine or pyran systems, the rate of increase of compressibility with saturation remains about the same (Fig. 1). In the five-membered rings, however, no such uniformity exists: furan has a greater compressibility than tetrahydrofuran, yet pyrrole's is smaller than that of pyrrolidine.

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[1] The opinions contained herein are the private ones of the writer and are not to be construed as official or reflecting the views of the Navy Department or the Navy Service at large. Article not copyrighted.

(2) Weissler, THIS JOURNAL, **70**, 1634 (1948); **71**, 93 (1949).

(3) Lagemann, McMillan and Woolsey, *J. Chem. Phys.*, **16**, 247 (1948).

(4) Lagemann, Woolf, Evans and Underwood, THIS JOURNAL, **70**, 2994 (1948).

(5) Burton, *J. Acoust. Soc. Am.*, **20**, 186 (1948).

(6) Schaafs, *Z. physik. Chem.*, **A194**, 28–50, 66–85, 170–178 (1944).

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(8) Schaafs, *Ann. Physik*, **40**, 401 (1941).

TABLE I

PHYSICAL PROPERTIES OF CYCLIC COMPOUNDS AT 30°

Compound	Veloc. sound m./sec.	d, g./ml.	n_D	Molar sound velocity Obs.	Molar sound velocity Calcd.	Molar sound velocity Dev., %	Molar refraction Obs.	Molar refraction Calcd.	Molar refraction Dev., %	Compressibility[a] 10^{-12}
Benzene	1276.4	0.8685	1.4949	975.6	971.0	+0.47	26.22	26.37	−0.57	70.67
Cyclohexene	1254.5	.8023	1.4411	1113.8	1102.3	+1.03	27.04	27.31	−1.00	79.20
Cyclohexane	1229.1	.7692	1.4206	1172.0	1167.9	+0.35	27.72	27.78	−0.22	86.06
Dicyclohexyl	1422.3	.8790	1.4754	2127.6	2149.7	−1.04	53.30	53.43	−0.24	56.24
Cyclopentene	1160.3	.7606	1.4168	941.0	907.6	+3.55	22.51	22.68	−0.76	97.65
Cyclopentane	1182.3	.7350	1.4008	1008.9	973.3	+3.52	23.17	23.15	+0.09	97.33
Dicyclopentyl	1361.4	.8664	1.4634	1768.4	1760.4	+0.45	43.98	44.17	−0.43	62.27
Furan	1104.6	.926	1.4151	759.9	732.1	+3.66	18.41	19.35	−5.10	88.5
Tetrahydrofuran	1255.4	.8785	1.4020	885.4	863.4	+2.48	19.99	20.29	−1.50	72.23
Dihydropyran	1263.5	.9168	1.4362	991.9	992.4	−0.05	24.00	24.45	−1.87	68.32
Tetrahydropyran	1245.5	.8744	1.4157	1059.8	1058.0	+0.17	24.70	24.92	−0.89	73.72
Pyridine	1396.3	.9728	1.5045	908.6	908.2	+0.04	24.09	24.71	−2.57	52.73
Piperidine	1338.0	.8524	1.4474	1100.7	1101.1	−0.04	26.71	26.79	−0.30	65.53
Pyrrole	1438.3	.9578	1.5055	790.7	775.2	+1.96	20.79	21.22	−2.07	50.47
Pyrrolidine	1346.6	.8573	1.4360	916.1	906.5	+1.05	21.69	22.16	−2.17	64.33
Thiophene	1258.2	1.0523	1.5222	863.2	842.1	+2.45	24.39	25.03	−2.62	60.03
Thiazole	1372.3	1.1874	1.5339	796.7	779.3	+2.18	22.28	23.37	−4.89	44.72
1,4-Dioxane	1322.0	1.0215	1.4171	946.6	948.1	−0.16	21.69	22.06	−1.71	56.01
Morpholine	1423.4	0.9908	1.4501	989.1	991.2	−0.21	23.64	23.93	−1.27	49.81
1,4-Thioxane	1419.8	1.1070	1.5025	1057.6	1058.1	−0.05	27.79	27.74	+0.05	44.81
Tetralin	1447.8	0.9617	1.5379	1555.1	1563.4	−0.53	42.99	42.76	+0.53	49.61
Quinoline	1547.7	1.0851	1.6207	1376.8	1369.4	+0.54	41.85	40.16	+4.03	38.47

[a] Adiabatic compressibility 10^{-12} cm.^{2}/dyne.

Replacing a ring carbon by a nitrogen, oxygen, or sulfur always causes a decrease in compressibility, no matter whether the ring is five- or six-membered, saturated or unsaturated. Substitution of a second hetero atom gives a still further decrease as in dioxane, morpholine and thioxane; nitrogen and sulfur have a greater effect than oxygen. This behavior is related to the electrical forces between molecules due to the hetero atom.

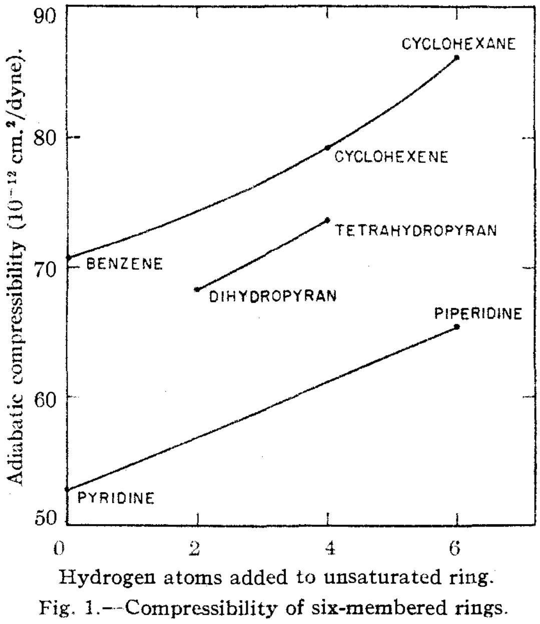

Fig. 1.—Compressibility of six-membered rings.

A compound which contains two rings has a lower compressibility than is associated with either of the individual rings.

Molar Sound Velocity.—Another useful quantity for studying the relation between molecular structure and sound velocity in liquids is the molar sound velocity R. This is defined[9] as the molar volume times the cube root of sound velocity

$$R = v^{1/3}M/d \qquad (2)$$

For most pure liquids, R is independent of temperature.

Like the molar refraction, R is an additive and constitutive property, which can be computed by summing the appropriate increments for all the bonds in the molecule. Some of the bond increments for molar sound velocity have been worked out by Lagemann.[10] These are listed in Table II,

TABLE II

BOND INCREMENTS FOR MOLAR CONSTANTS

Bond	Molar sound velocity	Molar refraction
C—H	95.2	1.69
C—C	4.25	1.25
C═C	129	4.16
C—O (in ethers)	44.5[a]	1.51
N—H	90.7[a]	1.81
C—N	20.7[a]	1.54
C═N	145[a]	3.90
C—S	99.5[a]	4.35[a]

[a] Previously unreported values, based on the present data and additional information from the literature.

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[9] Rao, *J. Chem. Phys.*, **9**, 688 (1941).

[10] Lagemann and Dunbar, *J. Phys. Chem.*, **49**, 434 (1945).

together with previously unreported values for the N–H, C–N, C=N, C–O (in ethers) and C–S bonds, which are derived from the present work and additional data from the literature. The last column of Table II gives the corresponding increments for molar refraction, as determined by Denbigh[11] and Warrick.[12]

The values for molar sound velocity and molar refraction calculated from these bond increments are compared in Table I with the values from the observed physical properties of the liquids. It is notable that five-membered rings show the larger deviations, especially in the molar velocity. The molar refractions show an average deviation of 1.6% between observed and calculated values, while the molar sound velocities show an average deviation of only 1.2%. In the present case, therefore, the molar sound velocity appears to be more useful than the molar refraction for structure investigations, by being less subject to such anomalies as are due to ring structure and conjugation of double bonds. This conclusion is to be employed with caution, particularly in view of the relatively small number of compounds studied here.

Acknowledgment.—The author is grateful to Dr. G. R. Ringo for stimulating discussions, and to the du Pont Company for samples of the furans and pyrans.

Summary

Through the use of a three-megacycle ultrasonic interferometer, the velocity of sound at 30° in twenty-two cyclic compounds has been determined. Densities and refractive indices at 30° are reported also.

Correlations have been found between molecular structure and sound velocity. For example, substituting nitrogen, oxygen or sulfur for a ring carbon causes a decrease in adiabatic compressibility.

For these liquids, the molar sound velocity is more nearly an additive property than the commonly-used molar refraction. It is possible, therefore, to predict the velocity of sound in pure liquids with an average accuracy of a few per cent., simply from the molecular structure and the density.

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[11] Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

[12] Warrick, THIS JOURNAL, **68**, 2455 (1946).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF POLAROID CORPORATION]

Polarographic Studies of Some Hindered and Unhindered Aromatic Nitro Compounds

BY MELVIN FIELDS,[1] CLAUDE VALLE, JR., AND MARSHALL KANE

Steric inhibition of resonance results in marked alterations of physical and chemical properties of organic molecules. Familiar examples of this phenomenon are the reduction of the dipole moments of nitromesitylene and nitrodurene from the values characteristic of aromatic nitro derivatives to approximately those of the aliphatic nitro compounds,[2] the striking alterations in the ultraviolet absorption of diphenyl derivatives[3] and of aromatic amines bearing bulky ortho substituents,[4] and the anomalous acid and base strengths of certain phenols, hydrocarbons and aromatic amines.[5] That the rates of chemical reactions may also be modified by the steric inhibition of resonance in a reacting molecule is illustrated by the numerous examples cited by Wheland.[6]

In this communication we wish to report on the results of a study of the effects of the steric inhibition of resonance on the polarographic characteristics of certain aromatic nitro compounds. Although the polarograph has been employed in the investigation of such varied phenomena as hydrogen bonding in nitrophenols[7] and in amidines,[8] semiquinone formation[9] and keto–enol tautomerism,[10] this instrument does not appear to have been utilized for the study of the effects of damped resonance on the properties of organic molecules. Suppression of the normal resonance of a reducible group with an aromatic nucleus might be expected to affect not only the ease of reduction but also the nature of the products of the reaction. In terms of the polarographic characteristics of a substance there might be observed a shift in the half-wave potential of a given stage of reduction, a change in the total number of electrons involved per molecule of electrode reaction or perhaps an alteration in the number of polarographic waves or distinct steps in which the over-all reaction occurs.

The substances which we studied were nitro-

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[1] Present address: Chemical Division, Tracerlab, Inc., Boston, Mass.

[2] Birtles and Hampson, *J. Chem. Soc.*, 10 (1937); Ingham and Hampson, *ibid.*, 981 (1939).

[3] Pickett, Walter and France, THIS JOURNAL, **58**, 2296 (1936); O'Shaughnessy and Rodebush, *ibid.*, **62**, 2906 (1940); and Williamson and Rodebush, *ibid.*, **63**, 3018 (1941).

[4] Remington, *ibid.*, **67**, 1838 (1945).

[5] Wheland, "The Theory of Resonance and its Application to Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 185.

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[7] Astle and McConnell, THIS JOURNAL, **65**, 35 (1943); Astle and Cooper, *ibid.*, **65**, 2395 (1943); Astle and Stephenson, *ibid.*, **65**, 2399 (1943).

[8] Runner, Kilpatrick and Wagner, *ibid.*, **69**, 1406 (1947).

[9] Müller, *Ann. N. Y. Acad. Sci.*, **40**, 91 (1940).

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