Novel Applications of Topological Indices.
1. Prediction of the Ultrasonic Sound Velocity in Alkanes and Alcohols

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Z. Naturforsch. **41 a,** 1238 – 1244 (1986); received December 13, 1985

Several different topological indices (the carbon number, the Wiener index, the Balaban distance sum connectivity index, the Randić molecular identification number, and the Randić molecular connectivity indices $^0\chi$, $^1\chi$, $^2\chi$, $^3\chi_p$ and $^3\chi_c$) were employed in the correlation of the velocity of ultrasonic sound in a variety of alkane and alcohol species. Using linear regression analyses and published sound velocity data, a number of excellent correlations were obtained for both alkanes and alcohols. Equations are developed which permit the prediction of sound velocity in these species to within 2% in most cases.

1. Introduction

Topological indices (TIs) are graph-theoretical invariants employed as molecular descriptors for the principal purpose of correlating and predicting a wide range of properties of molecular species. To date, approximately 100 different TIs have been put forward in the chemical literature [1], though only a handful of them have been widely used for correlative or predictive studies. Details of the more well-known TIs may be found in recent reviews on the subject [2–5]. Three books have also been devoted exclusively to the topic of TIs [6–8]. TIs have been used so far in the correlation and prediction of the physicochemical properties of species (e.g. boiling point [9], refractive index [10], solubility [11], and density [12]); the thermodynamic properties (e.g. heats of formation [13] and vaporization [14]); the biophysical properties (e.g. bioconcentration factor [15], biological degradability [16], and soil sorption [17]); and the physiological properties (e.g. carcinogenicity [18], and toxicity [19]). Studies have also been undertaken in which TIs have been employed in the characterization of molecular branching [20]; the correlation of σ- and π-electron energies [21–22]; the prediction of the energy gap in polymeric species [23]; the determination of the optimal positions of defect atoms in crystal lattices [24]; and the modelling of crystal growth processes [25].

In the present series of papers we propose to investigate novel applications of TIs for which no studies exist to date. Our main interest will focus on correlating and predicting the physicochemical and biophysical properties of molecular species. In this paper we start by correlating the velocity of ultrasonic sound in various members of two homologous series, viz. the alkanes, C_nH_{2n+2}, and the alcohols, $C_nH_{2n+1}OH$. Because of the broadly additive nature of sound velocities, it was anticipated that the ultrasonic velocity of members of homologous series (where there is a rough transferability of force constants between members) should correlate well with selected TIs. As we demonstrate below, this expectation has been amply corroborated.

The TIs selected for the purpose of this study were the number of carbon atoms in the species, n_C; the Wiener index, W (G) [26]; the distance sum connectivity index of Balaban, J (G) [27]; the molecular identification number of Randić, MID (G) [28]; and several of the molecular connectivity indices of Randić, namely $^0\chi$, $^1\chi$, $^2\chi$, $^3\chi_p$ and $^3\chi_c$ [6]. It was thought that this selection of TIs would provide a reasonable mix of indices known to characterize well molecular size (e.g. the carbon number and the Wiener index) and molecular branching (e.g. the Balaban distance sum connectivity index and the Randić molecular identification number). To calculate the TIs, appropriate computer programs were written; to take account of the oxygen heteroatom present in alcohol species, the correction described by Barysz et al. [19] was applied.

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2. Sound and Chemical Constitution

The frequency range of sound waves capable of stimulating the human ear is known as the audible range and lies between 20 Hz and 20 kHz. Frequencies below this range are referred to infrasonic and those above this range as ultrasonic. Our concern here will be with the latter frequency range which typically lies between 20 kHz and several MHz. The velocity of ultrasonic sound has been measured in a wide variety of liquids with the primary aim of determining their adiabatic compressibility. The experimental techniques for such measurements have included the use of the acoustic interferometer, the pulse technique, and optical diffraction [30]. The ultrasonic velocity of sound in a liquid, v, has been expressed [31] by the relationship:

$$v = [\varrho \cdot \beta_s]^{-\frac{1}{2}}, \tag{1}$$

where ϱ and β_s are, respectively, the density and adiabatic compressibility of the liquid at some temperature t °C.

The physical properties of liquids, such as their compressibility or density, can provide valuable information on both the molecular structure and the intermolecular forces present. Based on an approach of this type, Parthasarathy [32] concluded that the sound velocity in liquids could be related to their chemical constitution by the following general rules:

(i) In alkane, aliphatic alcohol and ketone species v increases as the chain length increases;
(ii) The higher the viscosity of a liquid the greater the value of v;
(iii) Liquids whose molecules have a dipole moment tend to display an enhanced v value;
(iv) The introduction of a heavier heteroatom into the molecule will reduce the v value;
(v) Among isomers, if the isomerism is not of the optical kind, there will be a difference in v values.

The results of this study led Parshad [33] to infer that the velocity of sound in liquids was an additive property.

This inference was later confirmed by Rao [34], who pointed out that the velocity of sound and liquid density were interrelated by the equation:

$$R = V v^{1/3} = \frac{m}{\varrho} v^{1/3}, \tag{2}$$

where R is Rao's constant, V the molecular volume at t °C, and m the molecular mass. Constitutional isomers were shown to possess identical R constants. Furthermore, the difference in R for successive members of an homologous series is also a constant which is independent of the type of compound. The R values for the atoms of interest to us here were reported [35] to be: $C = 10$; $H = 92.5$; and $O = 74$. Lagemann et al. [36] called R the 'molecular sound velocity' and devised a procedure for calculating R based on additive 'bond velocities'. In alkanes, for instance, the molecular sound velocity was determined for the expression $(n-1)(C-C) + (2n+2)(C-H)$, where the $C-C$ and $C-H$ values were found via a least squares procedure [36]. Similar results were obtained for velocities calculated from the atomic and bond values given by Rao [34].

3. The Effects of Hydrogen Bonding

In a study involving the lower members of the alkanes and monohydric alcohols, Lagemann and Dunbar [37] demonstrated that a linear relationship exists between molecular sound velocity and molecular refractivity, the parachor, Souder's viscosity constant, the van der Waals' b parameter, molecular magnetic rotation, and the critical volume. The slopes of the regression lines for both series were found to be almost identical (although the intercepts differed), suggesting that the effect of the greater hydrogen bonding present in the alcohols was not a very significant one. The agreement between the lines was so good that these workers postulated that a single regression line could be used to represent the data for both sets of compounds.

Weissler [38] investigated the correlation between the ultrasonic sound velocity and constitutional structure of 30 liquid alcohols by means of ultrasonic interferometry. He established that v increased with molecular mass (though not linearly) and decreased with the extent of branching present. Determinations were made of the molecular mass, the van der Waals' b parameter, and the adiabatic compressibility of these alcohols from the respective v values and appropriate combinations of physicochemical properties, such as the density or viscosity. An average error of 2% was obtained for the calculated molecular masses of the primary alcohols, with a greater deviation becoming apparent whenever the molecules were extensively branched. Only a fair result was achieved for the van der Waals' b parameter, whereas the adiabatic compressibilities agreed well with those published elsewhere. Weissler concluded that the adiabatic compressibilities decrease with molecular mass but increase with amount of branching.

The intermolecular potential energy, E_p, in normal $C_1 - C_{10}$ alcohols was calculated by Reddy [39] at several different temperatures using the equation:

$$E_{\mathrm{p}} = \frac{m\, v^2\, t\, \alpha}{\gamma}, \tag{3}$$

where α is the thermal expansion coefficient, γ the ratio of specific heats, and the other symbols have their previous significance. Comparison of the calculated E_{p} values with literature values of the heats of vaporization revealed that the latter were higher than the corresponding E_{p} values. The difference was attributed to the energy of association arising from hydrogen bond formation in the alcohols. The value for methanol at 298.15 K was equal to 25.26 kJ mol^{-1} and an average decrease of 1.2 kJ mol^{-1} was found for the addition of each methylene group. As might be inferred from the nature of hydrogen bonding, the hydrogen bond energy was shown to decrease with increasing alcohol chain length and also with increasing temperature.

4. Treatment of Data

Considerable difficulty was experienced in obtaining reliable data sets on which to perform our calculations. Values of v reported by different authors were found to differ in some cases by more than 10 m s^{-1}. With no convenient method of establishing the reliability of the reported data, our selection of data sets was necessarily somewhat arbitrary. For normal alkanes, v values for $C_5 - C_9$ species were taken from Bergmann [40] and for $C_{10} - C_{16}$ species from Petrova and Pichikyan [41]. In the case of branched alkanes, all the data were abstracted from Geelen et al. [42], except for the C_6 and C_9 species which were taken from Awwad and Pethrick [43]. The alcohol data were derived from the work of Weissler [38]. The temperature at which v was recorded for the alkanes was 20 °C whereas that for the alcohols was 30 °C.

For both the alkane and alcohol data sets, linear regression analyses were performed using each of the topological indices n_C, W (G), J (G), MID (G), ${}^0\chi$, ${}^1\chi$, ${}^2\chi$, ${}^3\chi_{\mathrm{p}}$ and ${}^3\chi_{\mathrm{c}}$ in turn. Separate linear regressions were also carried out on the normal and branched species in each case to determine how well the TIs were able to characterize branched species. In an attempt to improve upon the results obtained, multiple regression analyses were also carried out on our data sets, with up to three different TIs being employed simultaneously. The best results achieved from both the linear and multiple regression analyses are reported below.

5. The Alkane Results

For the data set of 35 alkanes studied, the best descriptor for the ultrasonic velocity, v, was found to be the reciprocal of the ${}^1\chi$ index. The linear regression equation obtained assumed the form:

$$v = 1503.57\,(\pm 111.85) - \frac{1206.72\,(\pm 2.23)}{{}^1\chi} \tag{4}$$

with $n = 35$, $r = 0.9523$, $s = 21.93$, $F_{1,33} = 321.08$. The observed and calculated ultrasonic velocities are presented together with the ${}^1\chi$ values in Table 1. The plot of v against $1/{}^1\chi$ is shown in Figure 1. Using a forward stepwise technique, the best multiple regression analysis result was found to be:

$$v = 1569.15\,(\pm 21.95) - \frac{1425.6\,(\pm 117.6)}{{}^1\chi} + \frac{3414.0\,(\pm 744.5)}{\mathrm{W}} - \frac{93.9\,(\pm 13.6)}{{}^3\chi_{\mathrm{p}}} \tag{5}$$

with $n = 35$, $r = 0.9834$, $s = 13.48$, $F_{3,31} = 301.7$. The correlation matrix for the three descriptors is given in Table 2.

For the subset of 9 normal alkanes, the best TI for characterizing ultrasonic velocity was J:

$$v = -72.68\,(\pm 32.35) + 1373.07\,(\pm 34.43)\ln \mathrm{J} \tag{6}$$

with $n = 9$, $r = 0.9978$, $s = 7.98$, $F_{1,7} = 1590.80$. The subset of 26 branched alkanes was best characterized by ${}^3\chi_{\mathrm{p}}$ according to the equation:

$$\frac{1000}{v} = 0.79\,(\pm 0.01) + \frac{0.130\,(\pm 0.015)}{{}^3\chi_{\mathrm{p}}} \tag{7}$$

with $n = 26$, $r = 0.8747$, $s = 0.015$, $F_{1,24} = 78.19$. The plot of $1000/v$ against $1/{}^3\chi_{\mathrm{p}}$ is shown in Figure 2. By

Table 1. Ultrasonic sound velocity in alkanes at 20 °C.

No.	Compound	$^1\chi$	Observed v [a] m s^{-1}	Calculated v [b] m s^{-1}	Difference
1	n-C_5	2.4142	1008	1003.7	4.3
2	n-C_6	2.9142	1083	1089.5	−6.5
3	n-C_7	3.4142	1162	1150.1	11.9
4	n-C_8	3.9142	1197	1195.3	1.7
5	n-C_9	4.4142	1248	1230.2	17.8
6	n-C_{10}	4.9142	1264	1258.0	6.0
7	n-C_{11}	5.4142	1289	1280.7	8.3
8	n-C_{13}	6.4142	1310	1315.4	−5.4
9	n-C_{16}	7.9142	1358	1351.1	6.9
10	2-MeC_5	2.7701	1070	1067.9	2.0
11	3-MeC_5	2.8081	1099	1073.8	25.2
12	2-MeC_6	3.2701	1121	1134.5	−13.5
13	3-MeC_6	3.3081	1145	1138.8	6.2
14	3-EtC_5	3.3461	1170	1142.9	27.1
15	2,2-Me_2C_5	3.0607	1086	1109.3	−23.3
16	2,3-Me_2C_5	3.1807	1150	1124.2	25.8
17	2,4-Me_2C_5	3.1259	1073	1117.5	−44.5
18	3,3-Me_2C_5	3.1213	1130	1117.0	13.0
19	2,3,3-Me_3C_4	2.9434	1105	1093.6	11.4
20	2-MeC_7	3.7701	1157	1183.5	−26.5
21	3-MeC_7	3.8081	1186	1186.7	−0.7
22	3-EtC_6	3.8461	1193	1189.8	3.2
23	2,2-Me_2C_6	3.5607	1135	1164.7	−29.7
24	2,3-Me_2C_6	3.6807	1181	1175.7	5.3
25	2,4-Me_2C_6	3.6639	1150	1174.2	−24.2
26	2,5-Me_2C_6	3.6259	1133	1170.8	−37.8
27	3,3-Me_2C_6	3.6213	1164	1170.3	−6.3
28	3,4-Me_2C_6	3.7187	1201	1179.1	21.9
29	2-Me-3-EtC_5	3.7187	1187	1179.1	7.9
30	3-Me-3-EtC_5	3.6820	1210	1175.8	34.2
31	2,2,3-Me_3C_5	3.4814	1167	1156.9	10.1
32	2,2,4-Me_3C_5	3.4165	1105	1150.4	−45.4
33	2,3,3-Me_3C_5	3.5040	1191	1159.2	31.8
34	2,3,4-Me_3C_5	3.5534	1181	1164.0	17.0
35	2,2,4-Me_3C_6	3.9772	1165	1200.2	−35.2

[a] Values for linear chains C_5-C_9 from [40], $C_{10}-C_{16}$ from [41] and values for branched chains C_6, C_9 from [43]; the rest are from [42].
[b] Calculated by Equation 4.

the expedient of eliminating from the analysis the three apparent outliers (shown as full points in Fig. 4), a much improved result can be obtained as follows:

$$\frac{1000}{v} = 0.78\ (\pm\,0.03) + \frac{0.135\ (\pm\,0.001)}{^3\chi_p} \qquad (8)$$

with $n = 23$, $r = 0.9637$, $s = 0.008$, $F_{1,21} = 273.84$. The observed and calculated ultrasonic velocities in branched alkanes are presented in Table 3.

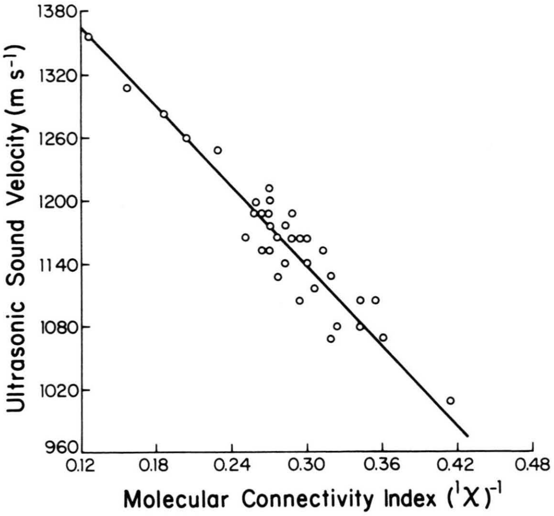

Fig. 1. Plot of the velocity of sound at 20 °C against $1/^1\chi$ for 35 different alkane molecules.

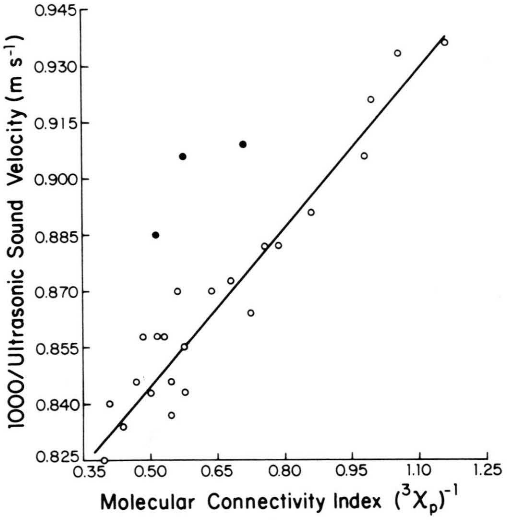

Fig. 2. Plot of 1000/velocity of sound at 20 °C against $1/^3\chi_p$ for 26 branched alkane molecules.

Table 2. Correlation matrix of descriptors in Equation (5).

	1/W	$1/^1\chi$	$1/^3\chi_p$
1/W	1.0000		
$1/^1\chi$	0.9530	1.0000	
$1/^3\chi_p$	0.7288	0.7105	1.0000

Table 3. Observed and calculated values of ultrasonic sound velocities in branched alkanes at 20 °C.

No.	Compound	Observed v m s^{-1}	Calculated v[a] m s^{-1}	Difference
1	2-MeC$_5$	1070	1116.0	−46.0
2	2-MeC$_6$	1121	1072.4	48.6
3	3-MeC$_6$	1145	1021.5	123.5
4	3-EtC$_5$	1170	986.9	183.1
5	2,2-Me$_2$C$_5$	1086	1093.9	−7.9
6	2,3-Me$_2$C$_5$	1150	980.4	169.6
7	2,4-Me$_2$C$_5$	1073	1103.2	−30.2
8	2-MeC$_7$	1157	1034.9	122.1
9	3-MeC$_7$	1186	984.9	201.1
10	3-EtC$_6$	1193	971.4	221.6
11	2,2-Me$_2$C$_6$	1135	1050.3	84.7
12	2,3-Me$_2$C$_6$	1181	975.4	205.6
13	2,4-Me$_2$C$_6$	1150	1008.6	141.4
14	2,5-Me$_2$C$_6$	1133	1044.2	88.8
15	3,3-Me$_2$C$_6$	1164	967.3	196.7
16	3,4-Me$_2$C$_6$	1201	922.0	279.0
17	2-Me, 3-EtC$_5$	1187	953.8	233.2
18	3-Me, 3-EtC$_5$	1210	888.5	321.5
19	2,2,3-Me$_3$C$_5$	1167	941.8	255.2
20	2,2,4-Me$_3$C$_5$	1105	1090.5	14.5
21	2,3,3-Me$_3$C$_5$	1191	897.9	293.1
22	2,3,4-Me$_3$C$_5$	1181	940.3	240.7
23	2,2,4-Me$_3$C$_6$	1165	963.0	202.0

[a] Calculated by Equation (8).

Table 4. Observed and calculated ultrasonic sound velocities in aliphatic alcohols at 30 °C.

No.	Compound	Observed velocity[a] m s^{-1}	Calculated velocity[b] m s^{-1}	Difference
1	Methanol	1088.9	1062.5	26.4
2	Ethanol	1127.4	1114.5	12.9
3	*n*-Propanol	1193.2	1162.1	31.1
4	*n*-Butanol	1225.3	1199.9	25.4
5	*n*-Pentanol	1254.8	1231.5	23.3
6	*n*-Hexanol	1288.6	1258.7	29.9
7	*n*-Octanol	1331.9	1304.2	27.7
8	*n*-Decanol	1363.8	1341.5	22.3
9	*n*-Dodecanol	1388.0	1373.2	14.8
10	Isopropanol	1125.2	1146.2	−21.0
11	Isobutanol	1176.5	1189.8	−13.3
12	*s*-Butanol	1196.8	1189.8	7.0
13	*t*-Butanol	1101.6	1169.1	−67.5
14	Isopentanol	1220.4	1222.9	−2.5
15	*t*-Pentanol	1180.4	1209.7	−29.3
16	2-Methylbutanol	1225.3	1225.2	0.1
17	3-Pentanol	1223.7	1225.2	−1.5
18	2-Ethylbutanol	1277.0	1255.2	21.8
19	4-Methyl-2-pentanol	1201.3	1243.5	−42.2
20	2-Heptanol	1266.8	1276.1	−9.3
21	2,4-Dimethyl-3-pentanol	1241.1	1265.7	−24.6
22	5-Ethyl-2-nonanol	1326.5	1351.1	−24.6

[a] From Ref. [38]. – [b] Calculated by Equation (9).

6. The Alcohol Results

For the data set of 22 primary alcohols, the best overall descriptor for correlating v was $^1\chi$ according to the equation:

$$\ln v = 6.97\ (\pm\ 0.01) + 0.14\ (\pm\ 0.01) \ln {}^1\chi \qquad (9)$$

with $n = 22$, $r = 0.9401$, $s = 0.023$, $F_{1,20} = 152.14$. The observed and calculated ultrasonic velocities for this set of alcohols are given in Table 4. The plot of $\ln v$ against $\ln {}^1\chi$ is shown in Figure 3. For linear alcohols it was found that either $^1\chi$ or $^3\chi_p$ could be used to characterize v:

$$v = 1081.15\ (\pm\ 10.94) + 166.35\ (\pm\ 0.67) \ln {}^1\chi \qquad (10)$$

with $n = 9$, $r = 0.9985$, $s = 6.13$, $F_{1,7} = 2255.13$; or

$$\ln v = 7.144\ (\pm\ 0.001) + 0.092\ (\pm\ 0.002) \ln {}^3\chi_p \qquad (11)$$

with $n = 7$, $r = 0.9987$, $s = 0.003$, $F_{1,5} = 1944.56$.

In the case of the subset of 13 branched alcohols, the best independent variable was found to be $^3\chi_p^v$ thus:

$$v = 1134.62\ (\pm\ 30.62) + 85.57\ (\pm\ 1.79)\ {}^3\chi_p^v \qquad (12)$$

with $n = 13$, $r = 0.9424$, $s = 21.13$, $F_{1,11} = 87.28$. The plot of v against $^3\chi_p^v$ is presented in Fig. 4. The observed and calculated ultrasonic velocities for the branched alcohols are given in Table 5.

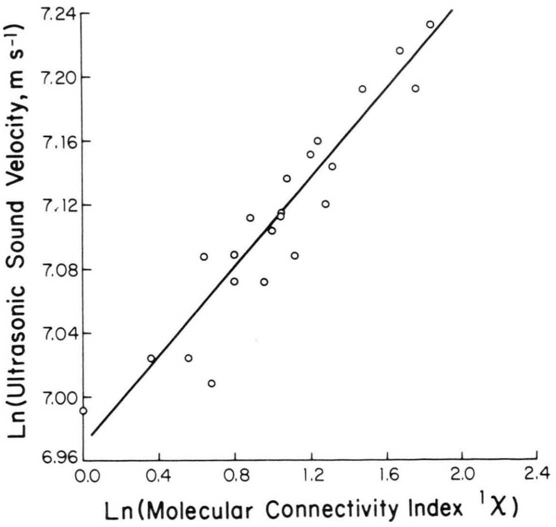

Fig. 3. Plot of natural logarithm of the velocity of sound at 30 °C against natural logarithm of $^1\chi$ for 22 primary alcohol molecules.

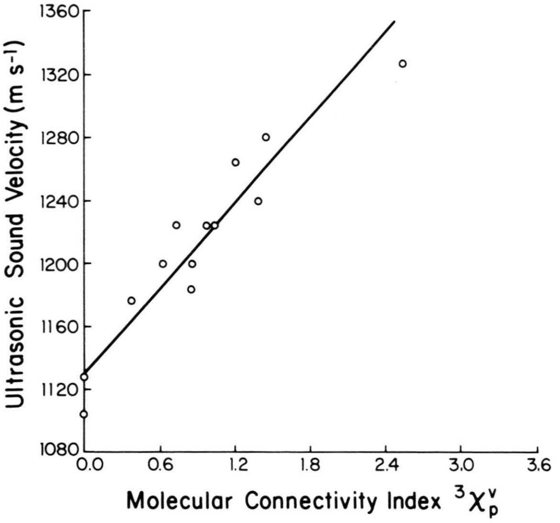

Fig. 4. Plot of velocity of sound at 30 °C against ${}^3\chi_p^v$ for 13 branched primary alcohol molecules.

Table 5. Observed and calculated ultrasonic velocities of branched alcohols at 30 °C.

No.	Compound	Observed velocity ms^{-1}	Calculated velocity[b] ms^{-1}	Difference
1	Isopropanol	1125.2	1134.6	−9.4
2	Isobutanol	1176.5	1165.9	10.6
3	*s*-Butanol	1196.8	1185.2	11.6
4	*t*-Butanol	1101.6	1134.6	−33.0
5	Isopentanol	1220.4	1200.6	19.8
6	*t*-Pentanol	1180.4	1208.6	−28.2
7	2-Methylbutanol	1225.3	1220.9	4.4
8	3-Pentanol	1223.7	1215.3	8.4
9	2-Ethylbutanol	1277.0	1255.5	21.5
10	4-Methyl-2-pentanol	1201.3	1204.1	−2.8
11	2-Heptanol	1266.8	1239.5	27.3
12	2,4-Dimethyl-3-pentanol	1241.1	1251.5	−10.4
13	5-Ethyl-2-nonanol	1326.5	1351.6	−25.1

[b] Calculated by Equation (12).

7. Discussion of the Results

For both the alkane and alcohol species studied, the molecular connectivity indices ${}^1\chi$ and ${}^3\chi_p$ yield the best correlations. This suggests that for transmission of sound at ultrasonic frequencies, paths of lengths one and three are especially important in the molecular graphs considered. Neither index is unique and in the case of ${}^1\chi$, for instance, the molecules of 3,4-dimethylhexane and 2-methyl-3-ethylpentane possess identical ${}^1\chi$ values. In general, ${}^1\chi$ values increase by one half for each succeeding member of any homologous series. However, whereas ${}^0\chi$ and ${}^2\chi$ values increase with the amount of branching present in species having a fixed number of carbon atoms, ${}^1\chi$ decreases with branching [6]. Thus, although ${}^0\chi$, ${}^1\chi$ and ${}^2\chi$ encode similar types of information for tree graphs, ${}^1\chi$ should yield the best correlation since increasing the amount of branching in molecular species is known to decrease the velocity of sound travelling through them. The negative sign in front of the ${}^1\chi$ term in (4) precisely reflects this type of relationship. The index ${}^3\chi_p$ follows the same trend with increasing amount of branching, and so in (5) it too is preceded by a negative sign.

In going from (4) with one independent variable to (5) having three such variables it may be noted that there is a significant reduction in the standard deviation and a marginal improvement in the correlation coefficient for alkane species. The one variable model is clearly much easier to apply in practice, and since the overall results are not substantially improved, it appears that perhaps the much simpler Eq. (4) is to be preferred to (5). For this reason multiple correlations were not attempted in the case of alcohols. Much better results can be achieved using single variables by omitting outlying points from the correlations. This is evidenced by Fig. 2 which includes three outlying points shown as full points. When these three points were eliminated from the study, the correlation coefficient increased from 0.8747 to 0.9637. The method we have used can therefore be reliably used to detect suspect data points. It is also anticipated that ultrasonic sound data for higher temperatures will yield better correlations. This is because molecules become increasingly free to rotate and generally to behave more independently of one another as the temperature rises. It was not possible to check on this owing to a paucity of appropriate data at higher temperatures. The effect should be more pronounced in the alcohols than in the alkanes owing to the greater degree of hydrogen bonding present in the former species.

In unbranched species it was found that all of the TIs employed here correlated well with ultrasonic sound velocity. This doubtless occurs because all the TIs reflect the size of the molecule and the sound velocity is known to increase in a regular, though not constant, fashion with molecular size. Modelling the observed trends in the branched species, however, proved to be much more difficult. Examples of such trends are that higher sound velocities are associated with more symmetrical molecules and also with isomers having 3-substitution rather than 2-substitution. The Balaban J index, which in general provides a sensitive measure of molecular branching, proved to be disappointing. Whereas J was the best for characterizing the sound velocities in normal alkanes, it showed no correlative power ($r = 0.0599$) for branched alkane species, even after various data transformations had been performed. The best TIs for the branched species – ${}^3\chi_p$ for alkanes and ${}^3\chi_p^v$ for alcohols – still led to quite large deviations between the observed and calculated sound velocities, as is evident from Tables 3 and 5. These results suggest that of the TIs used in this study none is completely satisfactory to model branched species. More sensitive branching indices than those applied here will therefore need to be used in future.

Acknowledgement

We are indebted to the U.S. Office of Naval Research for partial support of this research project.

[1] D. H. Rouvray and C. Raychaudhury, J. Comp. Chem., in press.
[2] I. Motoc, A. T. Balaban, O. Mekenyan, and D. Bonchev, Math. Chem. **13,** 369 (1982).
[3] A. T. Balaban, I. Motoc, D. Bonchev, and O. Mekenyan, Topics Curr. Chem. **114,** 21 (1983).
[4] D. H. Rouvray, in: Chemical Applications of Topology and Graph Theory, ed. R. B. King, Elsevier, Amsterdam 1983, p. 159.
[5] N. Trinajstić, Chemical Graph Theory, CRC Press, Boca Raton, Florida, 1983, Chapt. 4, p. 105.
[6] L. B. Kier and L. H. Hall, Molecular Connectivity in Chemistry and Drug Research, Academic Press, New York 1976.
[7] D. Bonchev, Information-Theoretic Indices for Characterization of Chemical Structures, Research Studies Press, Chichester, U.K., 1983.
[8] A. T. Balaban and I. Motoc, Handbook of Topological Indices, CRC Press, Boca Raton, Florida, 1986.
[9] H. Wiener, J. Amer. Chem. Soc. **69,** 17, 2636 (1947).
[10] A. T. Balaban, Theor. Chim. Acta **53,** 355 (1979).
[11] L. H. Hall, L. B. Kier, and W. J. Murray, J. Pharm. Sci. **64,** 1974 (1975).
[12] L. B. Kier, W. J. Murray, M. Randić, and L. H. Hall, J. Pharm. Sci. **65,** 1226 (1976).
[13] M. Randić, J. Amer. Chem. Soc. **97,** 6609 (1975).
[14] J. R. Platt, J. Chem. Phys. **15,** 419 (1947).
[15] A. Sabljić and M. Protić, Chem.-Biol. Interactions **42,** 301 (1982).
[16] P. Beltrame, P. L. Beltrame, and P. Carniti, Chemosphere **13,** 3 (1984).
[17] A. Sabljić, J. Agric. Food Chem. **32,** 243 (1984).
[18] L. von Szentpály, J. Amer. Chem. Soc. **106,** 602 (1984).
[19] R. Koch, Chemosphere **11,** 925 (1982).
[20] D. H. Rouvray, Discr. Appl. Math., in press.
[21] O. Mekenyan, D. Bonchev, and N. Trinajstić, Math. Chem. **6,** 93 (1979).
[22] D. Bonchev, O. Mekenyan, and N. Trinajstić, Int. J. Quant. Chem. **17,** 845 (1980).
[23] D. Bonchev and O. Mekenyan, Z. Naturforsch. **35 A,** 739 (1980).
[24] O. Mekenyan, D. Bonchev, and H.-G. Fritsche, Z. Phys. Chem. **265,** 959 (1984).
[25] D. Bonchev, O. Mekenyan, and H.-G. Fritsche, J. Cryst. Growth **49,** 90 (1980).
[26] D. H. Rouvray, in: Applications of Mathematical Concepts to Chemistry, ed. N. Trinajstić, Ellis Horwood Publishers, Chichester, U.K. 1985, Chapt. 25, p. 295.
[27] A. Balaban, Chem. Phys. Lett. **89,** 399 (1982).
[28] M. Randić, J. Chem. Inf. Comput. Sci. **24,** 164 (1984).
[29] M. Barysz, G. Jashari, R. S. Lall, V. K. Srivastava, and N. Trinajstić, Studies Phys. Theor. Chem. **28,** 222 (1983).
[30] J. Blitz, Ultrasonics: Methods and Applications, Butterworths, London 1971.
[31] B. Carlin, Ultrasonics, McGraw-Hill, New York 1960, p. 19.
[32] S. Parthasarathy, Curr. Sci. **7,** 322 (1938).
[33] R. Parshad, Ind. J. Phys. **19,** 47 (1945).
[34] M. R. Rao, J. Chem. Phys. **9,** 682 (1941).
[35] M. R. Rao, Curr. Sci. **5,** 534 (1940); ibid **8,** 510 (1939).
[36] R. T. Lagemann and J. E. Corry, J. Chem. Phys. **10,** 759 (1942).
[37] R. T. Lagemann and W. S. Dunbar, J. Phys. Chem. **49,** 428 (1945).
[38] A. Weissler, J. Amer. Chem. Soc. **70,** 1634 (1948).
[39] K. S. Reddy, J. Acoust. Soc. India **9,** 9 (1981).
[40] L. Bergmann, Der Ultraschall, Hirzel-Verlag, Zürich 1954, p. 375.
[41] G. P. Petrova and N. A. Pichikyan, Vestnik Mosk. Univ. Fiz. **27,** 531 (1972).
[42] H. Geelen, H. I. Waterman, J. B. Westerdijk, and R. F. Klaver, Riv. Combust. **9,** 355 (1955).
[43] A. M. Awwad and R. A. Pethrick, J. Mol. Liquids **25,** 115 (1983).