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PROPERTIES OF TOPOLOGICAL INDICES AS STRUCTURAL PARAMETERS FOR COMPOUNDS CONTAINING OLIGOOXYETHYLENE CHAIN(S)

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SUMMARY

The application of different topological indices as structural descriptors is discussed for several groups of compounds exhibiting surface activity and potential extractants of metals. The influence of different structural fragments, such as alkyl groups, oligooxyethylene and/or thioethylene chains and heteroatoms, on the topological indices is discussed.

INTRODUCTION

Attempts to describe the structure of a compound by quantitative parameters led to the definition of several topological indices. Randič[1–4] and Kier and Hall[5,6] developed a system of molecular and valence molecular connectivity indices. These were extensively examined in quantitative structure–property (QSPR) or structure–activity (QSAR) relationships[7–14]. The application of molecular connectivity indices in correlation analysis was recently reviewed by Ekiert *et al.*[15].

Other topological indices are based on the concept of the molecular distance matrix. The Rouvray index[16], Wiener number[17] and Balaban index[18] have been considered as descriptors of structure. These parameters were first calculated for saturated hydrocarbons but the work of Balaban[18] allowed the range of compounds to be extended to unsaturated and aromatic hydrocarbons. Barysz *et al.*[19] reported on the construction of the distance matrix for graphs representing any molecular system, including systems containing heteroatoms.

Some studies on retention–structure[20–28] and polarity–structure relationships[29–35] have been published. The structures of examined compounds, such as liquid stationary phases in gas chromatographic columns, were described by using the numbers of characteristic fragments in their molecules. Some effect of neighbouring groups was also considered[36–39]. In many instances the description of the structure of a compound was rather qualitative[40,41].

The application of different topological indices to describe the structures of alkane and alkene molecules has been examined[42–44]. Kaliszan[45] stated that the connectivity index does not adequately reflect the retention index differences caused by

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varying unsaturation. This conclusion was confirmed in part, by Voelkel[44], when the use of dipole moment as a parameter of electric interactions was necessary in order to obtain satisfactory retention–structure correlations. Kaliszan[45] discussed the connectivity index as a useful descriptor of non-specific dispersive interaction increments of retention. If dispersion forces predominate (*i.e.*, on non-polar liquid stationary phases), the chromatographic behaviour of solutes could be explained by means of connectivity parameters. With polar stationary phases and/or solutes of varying polarity, the connectivity indices become of less importance for retention as the specific polar interactions predominate. However, as was shown for alkenes[44], the discriminating power of topological indices [I_B, $W(G)$, $R(G)$] is higher and they could probably much better act as a useful tool for compounds containing heteroatoms.

The aim of this paper is to discuss the usefulness of the examined parameters in describing the structures of a selected group of compounds with different structural elements. Such compounds exhibit surface-active properties and some are used as extractants of metals[29–35,45–47]. The application of the considered topological indices as structural parameters in the relationship between the polarity and structure of the examined compounds is considered below.

EXPERIMENTAL

Topological indices were calculated for four groups of compounds containing oligooxyethylene chain(s) in their molecules:

(a) oligooxyethylene glycol dialkyl ethers, $RO(CH_2CH_2O)_nR$ (**1**), where R = C_4H_9, C_8H_{17} or $C_{12}H_{25}$ and n = 3–9, and some of their sulphur analogues, $C_4H_9(OCH_2CH_2)_n(SCH_2CH_2)_mS(CH_2CH_2S)_m(CH_2CH_2O)_nC_4H_9$ (**2**), where m = 0–2 and n = 1–4;

(b) amino ether alcohols, $[R(OCH_2CH_2)_n]_2NCH_2CH_2OH$ (**3**), and their ethers, $[R(OCH_2CH_2)_n]_2N(CH_2CH_2O)_{n+1}H$ (**4**), where R = C_4H_9, C_6H_{13} or C_8H_{17} and n = 1–3;

(c) 1,3-bis[ω-alkoxyoligo(oxyethylene)]propan-2-ols, $RO(CH_2CH_2O)_nCH_2CH(OH)CH_2(OCH_2CH_2)_mR^1$ (**5**), where R = R^1 or R ≠ R^1 = C_4H_9, C_6H_{13} or C_8H_{17} and $n = m$ or $n \neq m$ = 0–4;

(d) oligooxyethylene derivatives of aliphatic alcohols, thio alcohols and alkylamines, $RX(CH_2CH_2O)_nR'$ (**6**), where R = C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$ or $C_{14}H_{29}$, R′ = H or CH_3, X = –O–, –S–, –NH–, =NCH_3 or =NC_4H_9 and n = 1–5.

For comparison, topological indices were also calculated for some linear and branched alkanes and some primary and secondary alcohols.

The molecular connectivity indices of the first ($^1\kappa$), second ($^2\kappa$) and third order ($^3\kappa$) and the appropriate valence molecular connectivity indices ($^1\kappa^v$, $^2\kappa^v$, $^3\kappa^v$) were calculated according to the procedures of Randič[1–4] and Kier and Hall[5,6].

The Rouvray index, $R(G)$, the Wiener number, $W(G)$, and the Balaban index, I_B, were calculated according to the procedures given by these authors, using the values of diagonal and off-diagonal elements of the distance matrix as given by Barysz *et al.*[19].

RESULTS AND DISCUSSION

A useful and sensitive structural parameter should describe any change in the structure of a molecule. The main structural elements present in the compounds discussed are alkyl groups of different length, oligooxyethylene and thioethylene chains(s) containing different numbers of oxy- or thioethylene units and heteroatoms.

The first step was to examine the properties of topological indices for alkanes. An increase in the alkane chain length increases all the topological indices considered, but the characteristics of the relationships between each topological index and the chain length differ. The connectivity indices of the first, second and third order increase linearly (Fig. 1) with increase in the alkane chain length and the slopes decrease with increase of the index order. The Balaban index increases asymptotically with increase in the alkane chain length whereas the relationship between the Wiener number and the alkane chain length is parabolic (Fig. 1). Appropriate equations are given in Table I. This observation is consistent with those of Balaban[18], who stated that for an increasing number of carbon atoms from n to ∞ the Balaban index increases to π. The relationship between the Rouvray index and the alkane chain length is similar to that for the Wiener number.

Exemplary values of topological and molecular connectivity indices calculated for polyoxyethylene glycol dialkyl ethers (**1**) and their sulphur analogues (**2**) are presented in Tables II and III, respectively.

An increase in the length of the alkyl chain in polyoxyethylene glycol dialkyl ethers influences the topological indices in a different way (Fig. 2). An increase in the alkyl chain length results in a decrease in the Balaban index. This parameter calculated for alkanes having a number of carbon atoms equal to the total number of atoms in compounds **1** increases with increase in the carbon number. The values of the Balaban index for the hydrocarbon analogues are much lower than those for compounds **1**. The

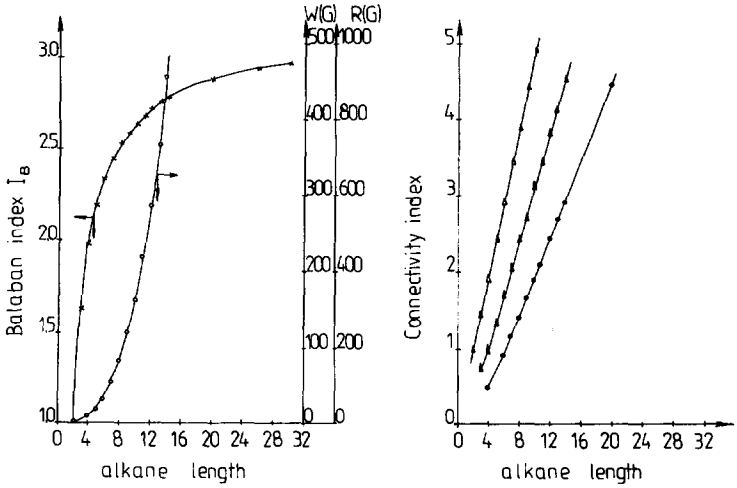

Fig. 1. Relationships between the topological indices and the length of the carbon chain in n-alkanes (n). ×, I_B *vs.* n; ○, $W(G)$ *vs.* n and $R(G)$ *vs.* n; △, $^1\kappa$ *vs.* n; ▲, $^2\kappa$ *vs.* n; ●, $^3\kappa$ *vs.* n.

TABLE I

RELATIONSHIPS BETWEEN THE TOPOLOGICAL INDICES AND THE NUMBER OF CARBON ATOMS FOR *n*-ALKANES ($N = 27$)

Topological index	*Equation*	*r*
I_B	$I_B = \pi(-1.3656/n + 0.9808)$	0.9348
$W(G)$	$W(G) = 1290.06 - 336.24n + 20.47n^2$	0.9965
$R(G)$	$R(G) = 645.03 - 168.12n + 10.23n^2$	0.9965
$^1\kappa$	$^1\kappa = -0.0742 + 0.5000n$	1.0000
$^2\kappa$	$^2\kappa = -0.4142 + 0.3535n$	1.0000
$^3\kappa$	$^3\kappa = -0.5429 + 0.25n$	1.0000

TABLE II

TOPOLOGICAL INDICES FOR POLYOXYETHYLENE GLYCOL DIALKYL ETHERS **1** AND THEIR SULPHUR ANALOGUES **2**

Group of compounds	*R*	*n*	*m*	*Balaban index, I_B*	*Wiener number, $W(G)$*	*Rouvray index, $R(G)$*
1	$C_{12}H_{25}$	3	–	3.2934	5990.5	11981
	$C_{12}H_{25}$	4	–	3.3480	7626.625	15325.25
	$C_{12}H_{25}$	5	–	3.3930	9540.25	19080.5
	$C_{12}H_{25}$	6	–	3.4314	11753.875	23507.75
	$C_{12}H_{25}$	7	–	3.4650	14290	28580
	$C_{12}H_{25}$	8	–	3.4896	17171.125	34342.25
1	C_8H_{17}	4	–	3.3880	3580.625	7161.25
	C_8H_{17}	7	–	3.5039	7886	15772
1	C_4H_9	4	–	3.4240	1310.625	2621.25
	C_4H_9	5	–	3.4730	1948.25	3896.5
	C_4H_9	6	–	3.5100	2765.875	5531.75
	C_4H_9	7	–	3.5380	3786	7572
	C_4H_9	8	–	3.5616	5031.125	10062.25
	C_4H_9	9	–	3.5805	6523.75	13047.5
2	C_4H_9	1	0	3.6092	443.5625	887.125
	C_4H_9	2	0	3.6800	1228.3125	2456.625
	C_4H_9	3	0	3.7128	2629.5625	5259.125
	C_4H_9	4	0	3.7280	4827.3125	9654.625
2	C_4H_9	1	1	4.2380	1077.1875	2154.375
	C_4H_9	2	1	4.1548	2370.4375	4740.875
	C_4H_9	3	1	4.0928	4433.1875	8866.375
	C_4H_9	4	1	4.0432	7445.4375	14890.875
2	C_4H_9	1	2	4.5812	2151.8125	4303.625
	C_4H_9	2	2	4.4610	4079.5625	8159.125
	C_4H_9	3	2	4.3662	6929.8125	13859.625
	C_4H_9	4	2	4.2900	10882.562	21765.125

TABLE III

MOLECULAR CONNECTIVITY INDICES FOR POLYOXYETHYLENE GLYCOL DIALKYL ETHERS 1 AND THEIR SULPHUR ANALOGUES 2

Group of compounds	*R*	*n*	*m*	*Molecular connectivity indices*			*Valence molecular connectivity index*		
				$^1\kappa$	$^2\kappa$	$^3\kappa$	$^1\kappa$	$^2\kappa$	$^3\kappa$
1	$C_{12}H_{25}$	3	–	16.9142	15.2236	11.6066	11.2234	15.2333	12.2222
	$C_{12}H_{25}$	4	–	18.4142	12.6673	8.7071	16.3010	10.4528	6.7725
	$C_{12}H_{25}$	5	–	19.9142	13.7279	9.4571	17.3783	11.0392	7.1445
	$C_{12}H_{25}$	6	–	21.4142	14.7886	10.2070	18.4557	11.6506	7.5165
	$C_{12}H_{25}$	7	–	22.9142	15.8492	10.9570	19.5330	12.2629	7.8885
	$C_{12}H_{25}$	8	–	24.4142	16.9099	11.7070	20.6104	12.8753	8.2605
1	C_8H_{17}	4	–	14.4142	9.8388	6.7071	12.3010	7.5974	4.7725
	C_8H_{17}	7	–	18.9142	13.0208	8.9571	15.5330	9.4345	5.8885
1	C_4H_9	4	–	10.4142	7.0104	4.7071	8.3010	4.7690	2.7725
	C_4H_9	5	–	11.9142	8.0711	5.4571	9.3783	5.3813	3.1445
	C_4H_9	6	–	13.4142	9.1317	6.2071	10.4557	5.9937	3.5165
	C_4H_9	7	–	14.9142	10.1924	6.9571	11.5330	6.6091	3.8885
	C_4H_9	8	–	16.4142	11.2530	7.7071	12.6104	7.2185	4.2605
	C_4H_9	9	–	17.9142	12.3137	8.4571	13.6877	7.8308	4.6325
2	C_4H_9	1	0	7.4142	4.8891	3.2071	7.9267	4.7644	2.9358
	C_4H_9	2	0	10.4142	7.0104	4.7071	9.4514	5.9891	3.6798
	C_4H_9	3	0	13.4142	9.1317	6.2071	11.6061	7.2139	4.4238
	C_4H_9	4	0	16.4142	11.2530	7.7071	13.7608	8.4386	5.1678
2	C_4H_9	1	1	10.4142	7.0104	4.7071	11.7521	8.4295	6.1560
	C_4H_9	2	1	13.4142	9.1317	6.2071	13.9068	9.6542	6.9000
	C_4H_9	3	1	16.4142	11.2530	7.7071	16.0615	10.8790	7.6441
	C_4H_9	4	1	19.4142	13.3744	9.2071	18.2162	12.1037	8.3881
2	C_4H_9	1	2	13.4142	9.1317	6.2071	16.2076	12.0946	9.3763
	C_4H_9	2	2	16.4142	11.2530	7.7071	18.3623	13.3193	10.1203
	C_4H_9	3	2	19.4142	13.3743	9.2071	20.5170	14.5440	10.8643
	C_4H_9	4	2	22.4142	15.4957	10.7071	22.6717	15.7688	11.6084

Wiener number, the Rouvray index and the connectivity indices increase with increase in the length of the alkyl chain, as was observed for saturated hydrocarbons. The values of $W(G)$ and $R(G)$ are lower than those obtained for corresponding hydrocarbon analogues. The connectivity indices do not distinguish between alkanes and compounds **1** having several oxygen atoms in the polyoxyethylene chain; the values of $^1\kappa$, $^2\kappa$ and $^3\kappa$ are the same for both groups of compounds. The use of valence molecular connectivity indices allows one to discriminate between these compounds; lower values were obtained for compounds **1**, although the trend of the connectivity index *vs.* alkyl chain length relationship remains unchanged.

The same relationships were observed between the topological indices and the number of carbon atoms in alkyl groups for compounds **3–6** (Fig. 3).

The change in the character of the relationships considered may be attributed to the presence of the oligooxyethylene chain. The Balaban index calculated for corresponding secondary and primary alcohols changes in a similar way as for

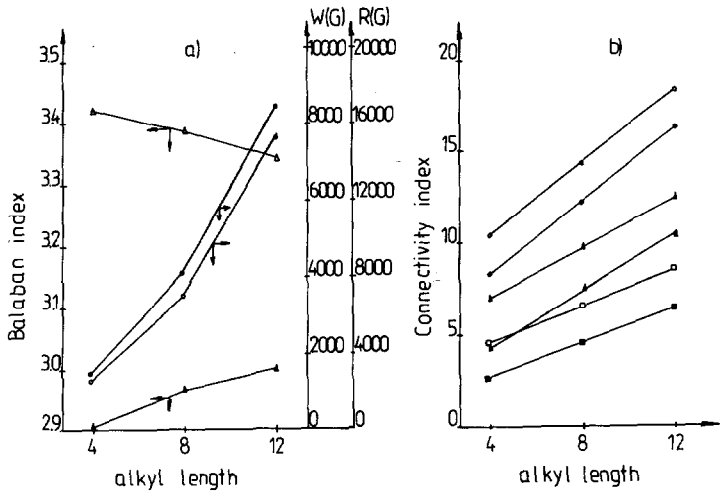

Fig. 2. Influence of the alkyl chain length (n) on the topological indices of polyoxyethylene glycol dialkyl ethers and their hydrocarbon analogues. (a) △,▲, I_B *vs.* n; ○,●, $W(G)$ *vs.* n and $R(G)$ *vs.* n; △,○, for compounds **1**: ▲,●, for alkane analogues of compounds **1**. (b) ○, $^1\kappa$ *vs.* n; ●, $^1\kappa^v$ *vs.* n; △, $^2\kappa$ *vs.* n; ▲, $^2\kappa^v$ *vs.* n; □, $^3\kappa$ *vs.* n; ■, $^3\kappa^v$ *vs.* n.

saturated hydrocarbons having the same number of atoms (Fig. 4). The term "alcohol analogue" denotes a primary or secondary alcohol corresponding to the examined compound in which all the ether oxygen atoms are replaced with methylene group, *e.g.*, an "alcohol analogue" for $ROCH_2CH(OH)CH_2(OCH_2CH_2)_2OR$ has the structure $RCH_2CH_2CH(OH)CH_2(CH_2CH_2CH_2)_2CH_2R$. However, higher values of the Balaban index were obtained for alcohols than alkanes.

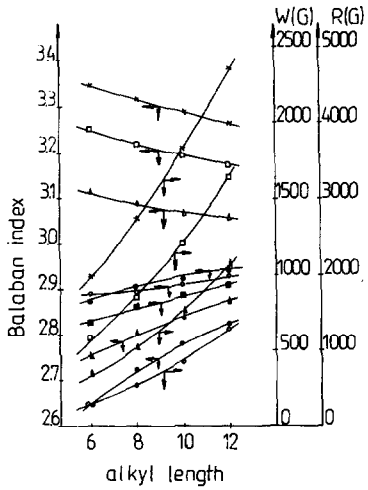

Fig. 3. Influence of alkyl chain length on the topological indices of oligooxyethylene derivatives of alcohols, $RO(CH_2CH_2O)_nR$. ○,●, For $n = 1$; △,▲, for $n = 2$; □,■, for $n = 3$; ×,⊗, for $n = 4$. ○,△,□,×, For oligooxyethylene alcohols; ●,▲,■,⊗, for their hydrocarbon analogues.

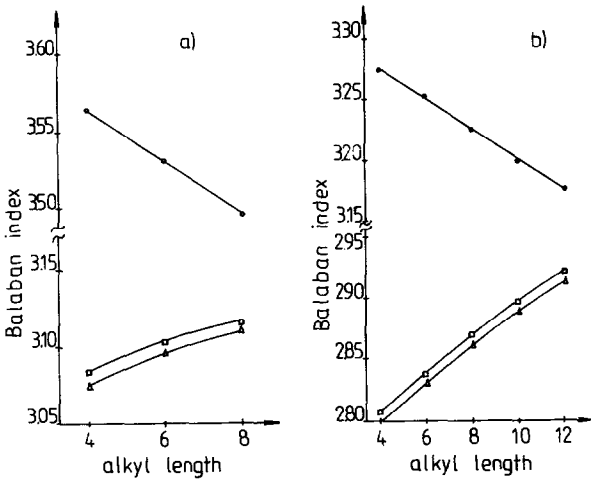

Fig. 4. Influence of alkyl chain length on the Balaban index of (a) $ROCH_2CH(OH)CH_2(OCH_2CH_2)_2R$ and (b) $RO(CH_2CH_2O)_3H$ and their (△) hydrocarbon and (□) "alcohol" analogues.

An increasing length of the oligooxyethylene chain in derivatives of aliphatic alcohols also significantly influences the relationship between the Balaban index and the alkyl chain length (Fig. 3). Other relationships such as those between the topological index and the alkyl chain length remain the same as above.

The important structural fragment in the molecules of the compounds examined is the oligooxyethylene chain. An increase in the oligooxyethylene chain length in compounds **1–6** increases all the topological indices discussed (Fig. 5). Only the relationships involving the connectivity indices have a linear character and $^1\kappa$, $^2\kappa$, $^3\kappa$ increase by 1.5, 1.0606 and 0.75 i.u., respectively, for each additional oxyethylene group.

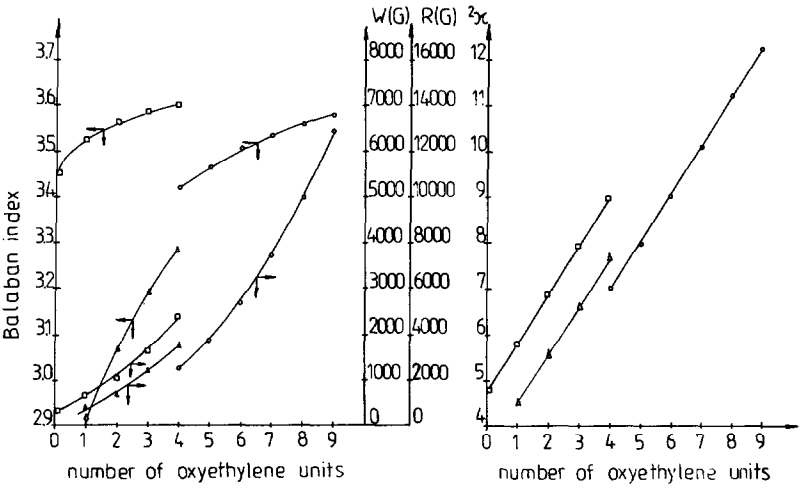

Fig. 5. Influence of the oligooxyethylene chain length on the topological indices for (○) $C_4H_9O(CH_2CH_2O)_nC_4H_9$, (△) $C_{10}H_{21}O(CH_2CH_2O)_nH$ and (□) $C_4H_9OCH_2CH(OH)CH_2O(CH_2CH_2O)_nC_4H_9$.

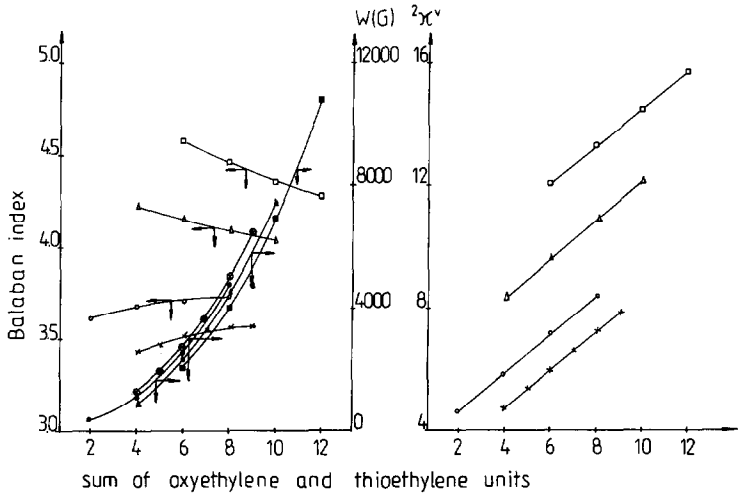

Fig. 6. Influence of the length of the hydrophilic chain on the topological indices for compounds **1** and **2**. ×,⊗, **1** (R=C_4H_9); ○,●, **2**, m = 0; △,▲, **2**, m = 1; □,■, **2**, m = 2. ×,○,△,□, For I_B and $^2\kappa^v$; ⊗,●,▲,■, for $W(G)$ and $R(G)$.

The replacement of oxygen with sulphur atoms (in compounds **2**) causes a decrease in polarity[29,30]. The more sulphur atoms in the molecule, the lower is the polarity exhibited by compounds **2** in comparison with their oxygen analogues **1**. As shown in Fig. 6, the Balaban index changes with increase in the hydrophilic chain length but the character of this relationship depends on the number of sulphur atoms present in the molecule. The same conclusion is valid for the molecular connectivity indices. The Wiener number and Rouvray index increase with increase in the number of sulphur atoms in compounds **2** (Fig. 7) when the length of the hydrophilic chain (the

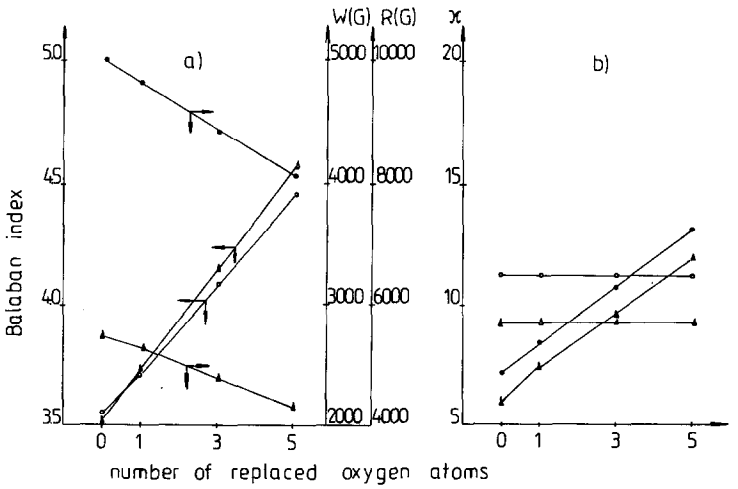

Fig. 7. Influence of the number of replaced oxygen atoms on the topological indices. △,▲, $n_{EO} + n_{ES}$ = 7; ○,●, $n_{EO} + n_{ES}$ = 9. △,○, For (a) I_B and (b) $^2\kappa$; ▲,●, for (a) $W(G)$, $R(G)$ and (b) $^2\kappa^v$.

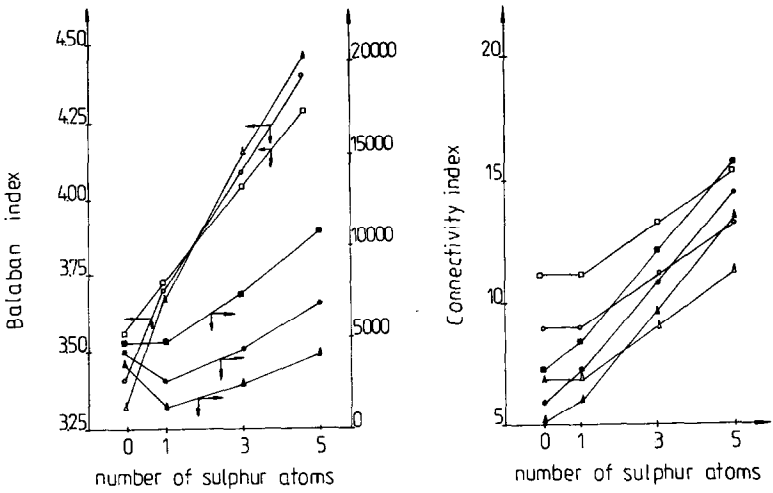

Fig. 8. Influence of the number of sulphur atoms on the topological indices. △,▲, $n_{EO} = 4$; ○,●, $n_{EO} = 6$; □,■, $n_{EO} = 8$. △,○,□, For I_B and $^2\kappa$; ▲,●,■, for $W(B)$ and $^2\kappa^v$.

sum of oxyethylene and thioethylene units) remains constant. The molecular connectivity indices do not change whereas the valence molecular connectivity indices increase with increase in the number of replaced oxygen atoms. An increase in the thioethylene chain length increases slightly the polarity of compounds **2**[29,30] when the number of oxyethylene units is constant (Figs. 7–9 in ref. 20). The replacement of the first oxygen with a sulphur atom causes a decrease in $W(G)$, whereas the introduction of each additional thioethylene unit increases $W(G)$ (Fig. 8). An analogues relationship is observed for the Rouvray index.

The location of a single sulphur atom in the molecule significantly influences the topological indices. The Balaban index decreases whereas the Wiener number and Rouvray index increase with increasing asymmetry of the molecule. The Wiener number and Rouvray index decrease in the order $Bu(OE)_2O(EO)_2Bu$ > $BuS(EO)_4Bu$ > $Bu(OE)S(EO)_3Bu$ > $Bu(OE)_2S(EO)_2Bu$ where Bu = C_4H_9, OE = OCH_2CH_2 and EO = CH_2CH_2O (Table IV).

TABLE IV

TOPOLOGICAL AND POLARITY PARAMETERS FOR ASYMMETRIC SULPHUR ANALOGUES

Compound[a]	*Topological indices*		*Polarity parameters*[29]	
	$W(G)$	I_B	$I_R^{C_2H_5OH}$	$pI^{C_2H_5OH}$ [b]
$Bu(OE)_2O(EO)_2Bu$	1310.625	3.4240	666.0	88.4
$BuS(EO)Bu$	1255.3125	3.5660	659.6	87.2
$Bu(OE)S(EO)_3Bu$	1235.0625	3.6480	653.7	85.7
$Bu(OE)_2S(EO)_2Bu$	1228.3125	3.6800	645.2	83.4

[a] Bu = C_4H_9; EO = $-OCH_2CH_2-$; EO = $-CH_2CH_2O-$.

[b] $pI^{C_2H_5OH}$ = Polarity index of ethanol as polar solute[29].

TABLE V

INFLUENCE OF THE DISTRIBUTION OF OLIGOOXYETHYLENE UNITS ON THE TOPOLOGICAL AND CONNECTIVITY INDICES FOR $C_4H_9O(CH_2CH_2O)_nCH_2CH(OH)CH_2(OCH_2CH_2)_m$-$C_4H_9$

n	m	*Topological indices*			*Molecular connectivity indices*					
		I_B	$W(G)$	$R(G)$	$^1\kappa$	$^2\kappa$	$^3\kappa$	$^1\kappa^v$	$^2\kappa^v$	$^3\kappa^v$
0	3	3.6025	2402.125	4804.25	12.8081	9.0465	6.3896	9.953	5.9602	3.5221
1	3	3.6425	2384.125	4768.25	12.8081	9.0465	6.3896	9.953	5.9602	3.5221
2	2	3.6550	2378.125	4756.25	12.8081	9.0465	6.3896	9.953	5.9602	3.5221

Compounds **3** also contain homologues with different lengths of both oligooxyethylene chains and different terminal alkyl groups. The influence of the asymmetry of the molecules on their polarity has been discussed previously[32]. The comparison of the values of the topological indices, when the influence of the distribution of the oxyethylene units is taken into account, is limited to compounds having the same total length of the oligooxyethylene chains and the same length and distribution of alkyl groups. The increasing asymmetry of the distribution of the oligooxyethylene units in the molecule decreases the Balaban index, whereas the Wiener number and Rouvray index increase (Table V).

The asymmetry of the hydrocarbon groups could be discussed for compounds having the same length and distribution of oligooxyethylene chains and the same number of carbon atoms in both alkyl groups. Appropriate data are presented in Table VI. The values of the Balaban index are lower for asymmetric compounds, whereas the Wiener number and Rouvray index increase slightly.

The molecular connectivity indices and valence molecular connectivity indices do not change with the increasing asymmetry of either the polar or apolar part of the molecule.

A change in the heteroatoms present in compounds **6** also influences their structural parameters (Fig. 9). The Balaban index, the Wiener number and the Rouvray index distinguish between derivatives of alcohols, alkylamines and thio alcohols. The highest I_B values were obtained for derivatives of thio alcohols and the

TABLE VI

INFLUENCE OF THE DISTRIBUTION OF CARBON ATOMS IN ALKYL GROUPS ON THE TOPOLOGICAL INDICES AND CONNECTIVITY INDICES FOR $RO(CH_2CH_2O)_nCH_2CH(OH)$-$CH_2(OCH_2CH_2)_mR^1$

n	m	R,R^1	I_B	$W(G)$	$R(G)$	$^1\kappa$	$^2\kappa$	$^1\kappa^v$	$^2\kappa^v$
0	0	$R = R^1 =$	3.4102	826.625	1653.25	2.8081	9.0465	9.953	5.9602
0	1	C_6H_{13}	3.4880	1299	2598	2.8081	9.0465	9.953	5.9602
1	1		3.5512	1922.875	3845.75	2.8081	9.0465	9.953	5.9602
0	0	$R = C_8H_{17}$,	3.3643	834.625	1669.25	2.8081	9.0465	9.953	5.9602
0	1	$R^1 = C_4H_9$	3.4680	1305	2610	2.8081	9.9465	9.953	5.9602
1	1		3.5236	1934.875	3869.25	2.8081	9.0465	9.953	5.9602

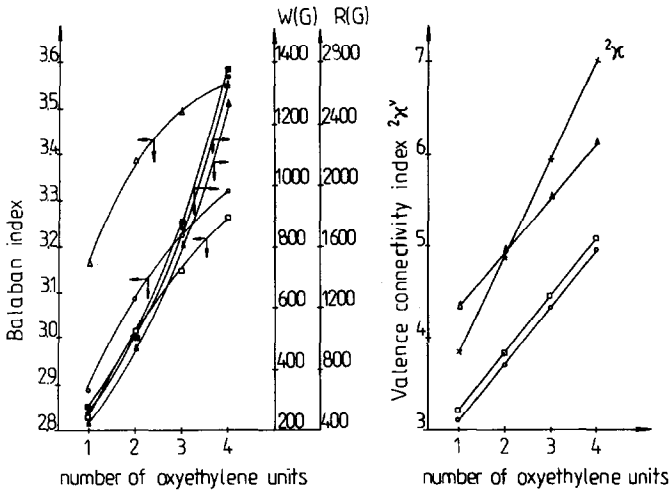

Fig. 9. Influence of the oligooxyethylene chain length on the topological indices for $C_8H_{17}X(CH_2CH_2O)_nH$. ○,●, X = –O–; △,▲, X = –S–; □,■, X = –NH–.

lowest for derivatives of alkylamines. The same values of the molecular connectivity indices $^m\kappa$ were obtained for all compounds **6**. The use of the valence molecular connectivity indices $^m\kappa^v$ allows one to distinguish between these derivatives. The values of $^2\kappa^v$ decrease in the order thio alcohols > alkylamines > alcohols.

CONCLUSIONS

The Balaban index, the Wiener number and Rouvray index seem to be the suitable parameters to describe the structure of a compound and could be used, for example, in the relationships between the structure and activity of the compounds examined. However, the topological parameters considered describe the structure of the compounds examined in different ways. These differences arise from the definitions of the topological indices. The Balaban index may be treated, from its definition, as the average distance between two vertices of a molecular graph. Other parameters are calculated as the sums of distances between vertices in the molecular graph, and therefore they increase with increasing number of adjacent atoms in the molecule. The possible variations of the Wiener number caused, for example, by the presence of an oligooxyethylene chain may be suppressed by the influence of the increasing molecular mass.

The Balaban index, increases with decrease in the alkyl length and increase in the oligooxyethylene chain length. The influence of a given structural element depends significantly on the presence and number of other structural fragments. Topological indices are sensitive to the asymmetry in the polar and hydrocarbon parts of the molecule. The replacement of one oxygen atom with sulphur or an NH group changes the Balaban index in the order derivatives of thio alcohols > alcohols > alkylamines. Of the group of connectivity indices, the valence molecular connectivity index is more suitable for such use than the molecular connectivity index, because the latter does not distinguish between different heteroatoms.

The question of which topological index differentiates best the individual structures of organic compounds remains open. One should take into account that graph theoretical descriptors have been designed for closely congeneric sets of compounds (linear and branched alkanes). Kier and Hall's and Barysz *et al.*'s modifications of topological indices lie outside the close graph theory and they include an electronic (the number of valency electrons) and not only a structural component. The discriminating power of a given topological index may be limited to an examined group of compounds. Therefore, the chromatographer looking for an appropriate structural parameter should select the one from the group of topological indices that best discriminates between the examined set of compounds.

The application of the considered topological indices as structural descriptors in retention–structure or polarity–structure relationships will be discussed in detail in subsequent papers. The retention–structure relationships for oligooxyethylene derivatives of alcohols, thio alcohols and alkylamines on standard stationary phases of different polarity will be discussed. The compounds considered in this paper and also others were used as liquid stationary phases and their polarity–structure relationships will be evaluated. As the compounds are of medium and relatively high polarity[29–35,48–50], it is expected that the future relationships will include not only topological indices but also parameters describing electrical and/or chemical properties of compounds.

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