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ON THE RELEVANCE OF ISOSPECTRAL NONISOMORPHIC GRAPHS FOR CHEMISTRY

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Summary

As far as is known so far, isospectral nonisomorphic graphs appear only if the hydrogens are neglected and if all bonds are equivalent and all atoms too, which is a rather unrealistic description of a chemical structure. More realistic descriptions of the chemical structure give for all inspected examples different eigenvalues of the topological matrices and therefore different invariants, so that in principle an application of such modified topological matrices to physicochemical problems is possible.

Introduction

A chemical compound is often described by its structural formula. Therefore it is tempting to use this structural formula not only for pure illustration but as starting point for thorough investigations, such as in the field of structure properties relations or documentation.

According to mathematics, the structural formula is a graph [1], i.e. a set of vertices or knots (atoms) which are connected by edges (bonds). After the first application of graph theory on chemical constitution by Cayley [2] in 1857, numerous publications on this topic appeared, comp [1]. An equivalent to these graphs exists in matrix theory, called topological matrices, which are symmetric and whose diagonal elements charcterize the atoms and the off-diagonal elements the bonds of the molecule. The application of topological matrices to conjugated π-electron systems is very common, and is known as Hueckel-theory [3].

For general molecules, Spialter [4] proposed topological matrices as an ideal and unequivocal representation of chemical structures, which are now used in documentation systems [5].

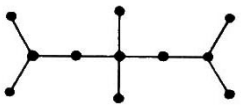
The one-to-one correspondence of a chemical structure and its graph or topological matrix is the essential basis for a useful application of this method for documention or for the investigation of structure property relations. To get rid off the fortuitous numeration in a mulecule, it is reasonable to discuss the

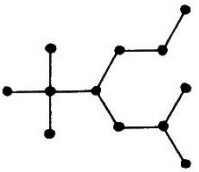
invariants of the corresponding topological matrix [6], e.g. most notably the eigenvalues. Under this circumstances it is disturbing to find in recent literature [7-14] pairs of isospectral nonisomorphic graphs, i.e. examples of distinctly nonisomorphic molecules which both have the same eigenvalue spectrum of their topological matrices and by this the same invariants. Since these findings make all the fine examples of application very dubious, we will investigate in the following the conditons for their appearance and their relevance to realistic applications.

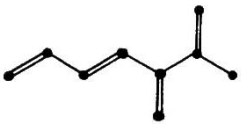
Method

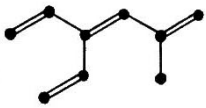
A closer inspection of the isospectral nonisomorphic graphs shows, that the commonly used graphs are an extremely rough description of a chemical structure: usually and without giving any reasons all vertices (atoms) as well as all edges (bonds) are equal and the hydrogen atoms are totally neglected, e.g. benzene and cyclohexane are equal. Considering these severe approximations, the occurrence of some difficulties is not completely surprising. Therefore we probed into some typical examples of pairs of isospectral nonisomorphic graphs from the literature, FIGURE 1. The topological matrices $\{Tij\}$ were defined by the following procedures:

I: only the connectivity of the main atoms was considered according to the literature [7-14]: $T_{ii} = 0$ for all i; $T_{ij} = 1$ if the atoms i and j are connected by a chemical bond; otherwise = 0;

1a 

1b 

2a 

2b 

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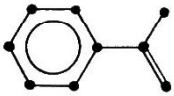
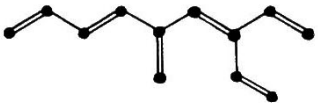
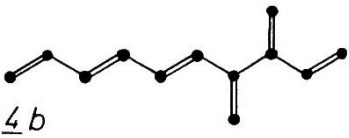
3b 

4a 

4b 

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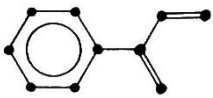
5b 

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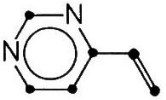

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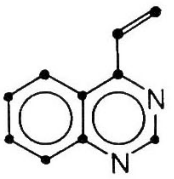

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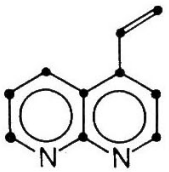

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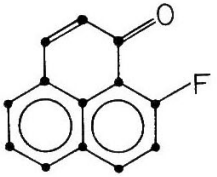

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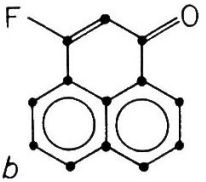

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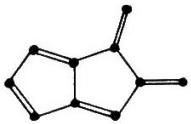

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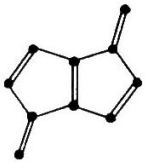

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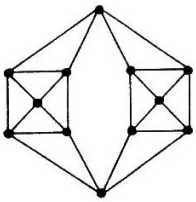

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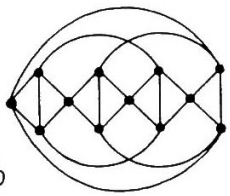

10b

Ia: same as I but including the hydrogen atoms;

II: be - matrices of Ugi [15] without hydrogens:

$T_{ii} = l_i$: number of lone pairs of electrons on atom i,

$T_{ij} = n_{ij}$: number of electron pairs in this bond,

i.e. $n_{ij} = \{0, 1, 1.5, 2, 3\}$;

IIa: same as II but including the hydrogen atoms;

III: classical Hueckel-calculations.

The procedures II and III are quite similiar in their structure but different in their numerical values. The procedure IIa is closer to the chemical structural formula than the other ones. Only the largest eigenvalues of the corresponding topological matrices are given in TABLE 1, since in these examples all the respective eigenvalues are equal if the largest are equal.

Discussion

TABLE 1 shows that by procedure I all pairs are isospectral in accordance with the literature [7-13].

But already in this crude method I the equality of the eigenvalue spectra disappears after the inclusion of the hydrogens, Ia, with the exeption of 8. This means that even the complete molecules (Ia) are with nearly no exception non isospectral! This equality disappears, too, if the description of the molecules corresponds more closely to the chemical structure as in II, IIa or III.

TABLE 1: Largest eigenvalues

Structure	Procedures				
	I	Ia	II	IIa	III
1a	2.2725	2.7944	2.2725	2.7944	
1b	2.2725	2.7938	2.2725	2.7938	
2a	2.0840	2.3957	2.9660	3.2241	2.3957
2b	2.0840	2.4003	3.0026	3.2435	2.2448
3a	2.1940	2.4843	3.1621	3.3656	2.3159
3b	2.1940	2.4791	3.1405	3.3620	2.3023
4a	2.1240	2.4266	3.0531	3.2986	2.0910
4b	2.1240	2.4201	3.0185	3.2815	2.0791
5a	2.2143	2.4944	3.1864	3.3989	2.1848
5b	2.2143	2.4875	3.1571	3.3824	2.1751
6a	2.1358	2.3877	3.4124	3.5471	2.2627
6b	2.1358	2.3767	3.4648	3.5880	2.2718
7a	2.3649	2.5241	3.7069	3.7848	2.4469
7b	2.3649	2.5217	3.7235	3.7976	2.4499
8a	2.5007	2.6238	3.7862	3.8362	3.2044
8b	2.5007	2.6238	3.7778	3.8301	3.2043
9a	2.4368	2.6078	3.3545	3.5117	2.3689
9b	2.4368	2.6084	3.3802	3.5231	2.3775

Somewhat more difficult is example 10 [14]. All atoms have the same number of connections (valence) and also the edges (bonds) could be equivalent in 10a and 10b respectively, so no differentiation is expected there and both graphs have the integer eigenvalues $\{4,2,2,2,0,0,0,-2,-2,-2\}$. The two graphs differ only by four connections, which are in one case the edges of a cube (10a) and in the other case the diagonals of a cube plane (10b); therefore they differ in length by a factor of $\sqrt{2}$. But this means that the bonds of 10a and 10b can not be chemically equivalent all together at the same time! By taking this into account and dividing these four bonds of 10b by any reasonable factor, the isospectral problem is eliminated, e.g. using the factor of $\sqrt{2}$ gives the spectrum $\{3.8, 2.2, 2.2, 1.7, 0, -.3, -.3, -1.7, -1.7, -1.9, -1.9, -2.1\}$ and 10a and 10b are no longer isospectral.

Conclusions

As we have shown, the isospectral nonisomorphic graphs known so far exist only because of the very crude simplifications in describing the chemical structure and they are consequently results of this very special approximation (I). Therefore one should be cautious when applying methods starting form this approximation (I), e.g. connectivity indices [17]. This paper does not refute the existence of abstract isospectral nonisomorphic graphs but demonstates that such an abstract graph is not a useful description of a chemical structure what so ever. In accordance with this conclusion is the first

experimental paper [18] about this topic, where the ionisation potentials of the isospectral pair 5 show no similarity with each other. Hence using an appropriate translation of the chemical structure into a topological matrix, the isospectral artifacts are of no relevance any longer and the topological matrices and their invariants can be meaningful tools for investigating chemical structures in physicochemistry.

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