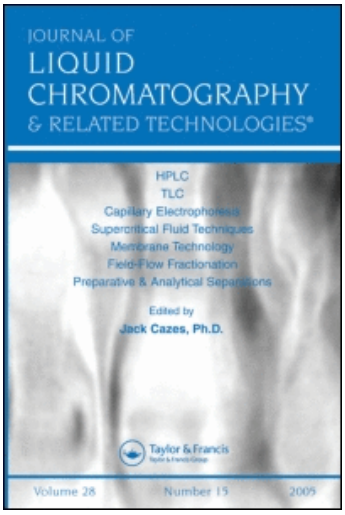

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PRELIMINARY STUDY ON THE RETENTION OF SOME ANTIOXIDANTS ON REVERSE PHASE THIN LAYER CHROMATOGRAPHIC PLATES

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PRELIMINARY STUDY ON THE RETENTION OF SOME ANTIOXIDANTS ON REVERSE PHASE THIN LAYER CHROMATOGRAPHIC PLATES

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ABSTRACT

The R_f values of ten antioxidants, namely several UOP, Permanax, Antozite, etc., have been calculated on the basis of their structures. The R_{fcalc} values have been compared with the experimental R_f values, obtained on reversed phase TLC plates. The variance of the calculated data around the experimental R_f values is $4 \cdot 10^{-4}$. The approach allows a positive identification without reference substances or with a limited number of standards, which is the structure that gives R_{fcalc} values close to the R_f of the sample spots. Some considerations on the probable retention mechanism are also given.

INTRODUCTION

The identification of the antioxidant spots on a TLC plate is performed mainly by comparison of the obtained R_f values with those of applied reference substances. Hence, a library of standards is necessary for reference. Even when this condition is fulfilled, a lot of applications are necessary. This is both expensive and time-consuming.

Table 1

Antioxidants, Their Trade Names and Abbreviations

	Antioxidant	Trade name	Abbreviation
1	N,N' Di-sec.butyl-p-phenylenediamine	UOP 5	D(secBu)PhDA
2	N,N' Di-2,4Dimethyl-amyl-p-phenylene-diamine	UOP788, Santoflex, Flexzone	D(DMAm)PhDA
3	N,N' Di-sec.heptyl-p-phenylenediamine	UOP 288 , Antozite 1	D(2MHp)PhDA
4	N,N'Di-2Ethyl-4methylamyl-p-phenylenediamine	UOP 88 , Antozite 2	D(2Et4MAm)PhDA
5	N,N' iPropyl-phenyl-p-phenylenediamine	Santoflex IP, Permanax IPPD, Flexzone 3C	iPrPhPhDA
6	N,N' sec. butyl-phenyl-p-phenylenediamine	Flexzone 5	secBuPhPhDA
7	N,N'2,4Dimethylbutyl-phenyl-p-phenylene-diamine	UOP 562, Antozite 67, Permanax 6PPD	24DMBuPhPhDA
8	N,N' sec. Octyl-phenyl-p-phenylenediamine	UOP 688	secOPhPhDA
9	N,N' Diphenyl-p-phenylenediamine	Permanax DPPD, Ekaland DPPD	DPhPhDA
10	N,N'Diphenylethylene-diamine		N,N'DPhEtDA

The so called Quantitative Structure-Retention Relationships (QSRR) concept allows calculation of the R_f values, based on the structure of expected antioxidants. According to the concept of QSRR the solute structure can be presented by the so called structure descriptors. Different solute properties as well as topological, geometrical, and/or quantum chemical indices have been used as descriptors. It is assumed, further, that one or a combination of descriptors can mimic the retention properties of the solute molecule. Thus, putting them as parameters in an equation, the value of the response (in this case, R_f) should approximate the experimental retention value.

If the difference between R_{fcalc} and R_{fexp} equals the laboratory repeatability, the identification is considered to be positive. If the identification is questionable, the practitioner can limit the number of reference substances

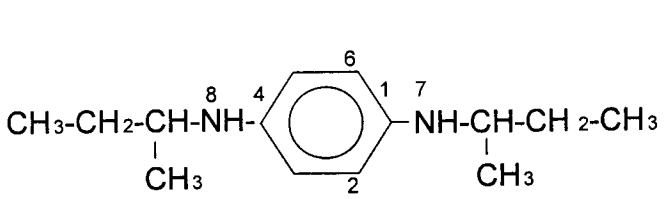

Figure 1. Structure of N,N'-di-sec.butyl-p-phenylenediamine and iso-propyl-phenyl-p-phenylenediamine, their molecular mass, Mm, number of C atoms in the substituents (in bracket - the number of C atoms in the straight chain), geometrical invariant of Winer index, GW, atom charge at C_2 atom in the ring and the electron population on the higher occupied molecular orbital (HOMO) of C^6 atom in the ring.

spotted on the sample plate, instead choosing structures, that give R_{fcalc} values which are close to the sample spot R_f values. The present work deals with the aforementioned screening process by means of 10 antioxidants separated on RP TLC plates.

EXPERIMENTAL

The experimental R_f values have been taken from the literature.[1] Compounds for which the accuracy of their predicted R_f value has been studied are given in Table 1. The hydrophobicity, logP, the total number of C atoms in alkyl chain(s), C_n, respectively, the length of straight chain, the molecular mass, Mm, the connectivity index, χ, Winer index, W, (topological indices), their geometrical and information invariance (e.g. GW, Info χ etc.) has been checked as defining the retention, taking into account the reversed character of the stationary phase. Based on our experience with RP stationary phases,

Table 2

Descriptors with the Highest Value of their Individual Correlation Coefficient, ir, Descriptors with Insignificant ir, but Tuning the Calculated R_f Value to an Experimental R_f Value

Descriptor	ir	Descriptor	ir
popHOMO{3}*	0.904	Planarity	0.36
Info χ	0.875	GIW	0.26
polar (3)	0.83	logP	0.26
popHOMO{1}, {2},{4},{5}	0.700-0.799	Q{2}	0.08
popHOMO{6}	0.671	popLUMO{j}	< 0.10

* The figure determines the atom number in the structure (see Figure 1).

contributions of the aromatic ring (e.g., the charge at a given ring C_i atom, Q{i}) and N atoms (e.g. population on j-orbital - popLUMO{j}) have also been tested. Two examples presented in Figure 1 explain qualitatively the meaning of some of the above mentioned structure descriptors. All calculations have been performed with the OASIS software program.[2,3]

To reduce the possibility of chance correlation, the model for creation of quantitative structure-retention relationship equations given elsewhere[4] has been used. Thus, only a few of all calculated indices have been tested as parameters in the equation for preliminary calculation of the solute retention.

RESULTS

Table 2 presents the descriptors with the highest individual correlation coefficient with the experimental retention. Results indicate that, the electron population on HOM orbital of ring C atom on ortho to -NH- location plays a significant role - the R_{fcalc} values correspond to a correlation coefficient r_i of 0.904 to those of R_{fexp}.

The R_{fcalc} is calculated by the aid of the following equation:

$$R_{fcalc}=0.52(\pm0.04)-1.53(\pm0.18).popHOMO\{3\} \quad (1)$$

(variance $v=3.10^{-3}$ and F = 74)

R_{fcalc} values are given in column 3 of Table 3. Although the r_i value is high, the accuracy is poor from a chromatographic point of view. The number of cases allows for the inclusion of two parameters in the equation.

Table 3

Comparison Between Experimental (R_{fexp}) and Calculated (R_{fcalc}) by Means of Equations 1 and 2 Retention Values

Abbreviation	R_{fexp}	R_{fcalc} Equ. 1	R_{fcalc} Equ. 2	pop HOMO {3}	pop HOMO {6}	Q{2}
DiBuPhDA	0.02	0.01	0.02	0.336	-0.1625	-0.0718
D(DMAm)PhDA	0.03	0.03	0.03	0.321	-0.1622	-0.0754
D(2MHp)PhDA	0.03	0.03	0.03	0.320	-0.1603	-0.0747
D(2Et4MAm)PhDA	0.11	0.005	0.11	0.338	-0.1817	-0.1288
iPrPhPhDA	0.08	0.18	0.08	0.222	-0.2240	-01657
secBuPhPhDA	0.14	0.19	0.10	0.216	-0.2167	-0.1652
24DMBuPhPhDA	0.19	0.21	0.19	0.202	-0.1881	-0.1643
secOPhPhDA	0.21	0.22	0.24	0.197	-0.1668	-0.1615
DPhPhDA	0.43	0.41	0.44	0.074	-0.0913	-0.1465
N,N'DPhEtDA	0.56	0.51	0.54	0.011	-0.240	-0.1088

The resultant expression is accurate:

$$R_{fcalc}=0.33(\pm0.02)+3.07(\pm0.12).popHOMO\{6\} -2.67(\pm0.18).Q\{2\} \quad (2)$$

with r_i = 0.9896, $v=4.10^{-4}$ and F = 334. The R_{fcalc} calculated by means of this equation R_{fcalc} values are given in column 4 of Table 3. The interrelation between what is used in the equation (2) parameters is statistically insignificant: 0.100.

DISCUSSION

This study gives information not solely for tentative, preliminary orientation about the identity of experimentally obtained spots. To rely on this information, equation (2) has been checked for chance correlation by the "leave-one-out" test. All parameter estimations of the 9 secondary equations are within the limits of parameter estimations of the equation (2).

Thus, equation (2) is accepted as reliable and is used for some considerations about the retention mechanism of studied amines on RP plates. It is usually assumed that, in reversed phase chromatography, the hydrophobicity is a very important factor. This study shows that the retention of amines studied

is independent of factors, immediately connected with the solution, for example, logP. It is also assumed that, for organic bases, the basicity of the N atom is also an important reason for the retention. As a result of the equations obtained, it follows that the local HOMO population is the significant factor for the retention. On the contrary, the population on LUM orbitals has a r_i with R_f below 0.1. Because the achieved accuracy with popHOMO{3} is not satisfactory, two descriptors have been combined. At combinations, popHOMO{6} is tuned better than popHOMO{3}. The best tuning parameter was the charge of $C^{(2)}$ ring atom. An adequate prediction has been achieved practically - the variance is $4 \cdot 10^{-4}$ and is statistically equal with the repeatability usually obtained in TLC. In conclusion, preliminary calculations of the R_f of expected compounds can make TLC work more effectively and can assist in formulating quantitative considerations of atomic interactions.

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REFERENCES

1. Ch. B. Airaudo, A. Gayte-Sorbier, P. Aujoulat, V. Mercier. *J. Chromatogr*., **437**, 59-82, (1988).

2. Ov. Mekenyan, S. Karabunarliev, D. Bonchev. *J. Math. Chem*., **4** 207-215 (1990), and Comput. Chem., **14**, 193-200 (1990).

3. Ov. Mekenyan, S. Karabunarliev, J. Ivanov, D. Dimitrov. *Comput. Chem*. **18**, 173-187 (1994).

4. Ov. Mekenyan, J. Ivanov, G. Veith, S. Bradbury. *Quant. Struct. Act. Relat*., **13**, 302-307 (1994).

5. N. Dimov. *J. Chromatogr*., **119**, 109-118 (1976).

6. N. Dimov, A. Osman. *Anal. Chim. Acta*, **323**, 15-25, (1996).

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