1-Naphthols as components for multifunctional material systems (MFMS): the molecular modeling approach

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Abstract

Increasing research interests have been paid to developing efficient multifunctional material systems (MFMS) by using various composite materials, owing to their useful properties and good stability. Here, we systematically studied 1-naphthols, especially how the type and position of a substituent influence the reactivity and properties, using different electron-directing groups. During computations, important preparation guidelines for thiol derivatives of 1-naphthol were obtained. It is very interesting to note that some molecules could exhibit intramolecular O–H–O interactions. Careful theoretical investigation reveals that all the tested compounds are stable and the molecules with substituents in positions 4 and 8 are the least reactive. It is also worth noting that for the stability and polarizability tensor values, it is more favorable when both substituents are in the same benzene ring. Among tested 1-naphthols, the greatest values of α , β , and γ are more than 5, 60, and 110 times better respectively, than in the urea molecule; the change of electron-withdrawing group (EWG) to electron-donating group (EDG) increases NLO effects. This study provided a new scope of 1-naphthols applicability by using them as anti-corrosion materials and as very good materials for NLO devices due to the high stability of the aromatic structure coupled with polarity given by the substituents. Also, the understanding of IR vibrations for more complex organic compounds with thiol substituent has been improved.

Keywords NLO · Substituent effect · DFT · MFMS components · Corrosion inhibition

Introduction

The composite materials are widely used in different areas of interest [59] including commercial implementations which is related to the possibility of obtaining the extreme properties which cannot be achieved by monolith bulk materials [23]; however, despite their good mechanical properties, they are very similar to other “common” materials acting only as building blocks. Thereby, the concept of introduction of extra functionalities of such materials has been proposed—in this way, materials could be more efficient (e.g., like the addition of self-cleaning property to a

construction built with a composite material)—through the approach of multifunctional material systems.

Multifunctional material systems (MFMS) are dedicated to exhibit additional functions (as energy accumulation, sensing, and others) apart from their primary functions associated with the mechanical properties as i.e. strength and stiffness [43, 65]. They are classified into multifunctional materials (MFM), multifunctional composites (MFC), and multifunctional structures (MFS) subgroups. The materials do not request new components, which is realized by combining one or more functional capabilities of constituents already present in the system.

Recently, the multifunctional composite materials have got attention due to their great potential of applications; hence, the research activity in the field is focused on looking for promising components (and functionalities) of such materials. There have been many different concepts proposed, among them the fluid-based actuation systems [14], microchanneled structures for biological usage [52], and composites showing crack surface repairing [62] (more detailed description and examples can be found in [43]).

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Here, we pay attention to 1-naphthols, one of the common groups of organic compounds used in the production of dyes [5, 11, 18, 25, 30, 34, 36, 49, 54] (including the green chemistry approach [6]), which have not been taken into account with regard to becoming the components of composite materials yet.

1-Naphthols are applied in a wide spectrum of interest: from using 2-alkyl-1-naphthol in hair-dyeing [29], through 2-nitroso-1-naphthol spectrophotometric detection of transition metals like ruthenium [32], palladium [13], and cobalt [15] to specific usage of polymers based on 1-naphthols. Especially, the polymerization of 5-amino-1-naphthol [1] is a very interesting aspect of 1-naphthol derivatives due to the corrosion protection possibility and ease of usage because of polyaniline-like structure. It was found that the poly(5-amino-1-naphthol) can be applied to form the film, which is semiconducting and exhibits reversible, well-defined oxidation-reduction response in both aqueous solutions of pH from 1 to 13 and protic non-aqueous solutions [44]. It is also possible to use unsubstituted 1-naphthol to form a polymer exploited as the sensitive, selective electrochemical sensor [35].

Based on their wide spectrum of implementations, it is clearly seen the 1-naphthols could represent quite interesting topic in relation to their potential of usage in MFMS. Besides the above-mentioned concepts of deployment, it is possible to find other functionalities of the group of organic compounds which may improve the properties of composite materials to be used in nonlinear optics (NLO) as materials for laser technology, data storage, and optical communication [58]. However, there is almost no data concerning nonlinear optical properties of any of 1-naphthols (so far the broader studies associated with the research scope have been developed by our group [8]), although they could be a promising object for the NLO field due to the planarity of the system provided by the aromatic ring of naphthalene and the possibility of charge transfer because of the presence of strong electron-donating hydroxyl group in the position 1 of the ring.

The electron transfer process could be also applied in the anti-corrosion treatment of organic molecules since it is based on the transfer of electrons between the studied molecule and structures forming a protected surface [42]. The type of a surface and in particular its charge distribution defining its chemical reactivity determine the properties of a prospective corrosion inhibitor. The question of the study is whether it is possible to obtain a corrosion inhibitor dedicated to the specific surface just by changing substituents in the 1-naphthol ring.

In this paper, some theoretical considerations concerning different substituents, their positions in the 1-naphthol ring, and their influence on different properties are taken into account. The influence of the position and type of the

substituent is considered, based on two different substituent types: electron-withdrawing (EWG) and electron-donating (EDG) groups, both having a moderate magnitude of EDG/EWG effect. Here, both types of EDG/EWG groups are studied for all possible positions in the aromatic ring to perform the analysis of their influence on the geometry of the aromatic ring, and determine the relative energies, reactivity descriptors for the prediction of the reactivity of each type of compound and substituent position. In this way, some predictions concerning an ability of corrosion protection and other applications associated with reactivity are performed. The final task is to calculate the values of polarizability and hyperpolarizability tensors to determine the potential of the 1-naphthol derivatives in the NLO field and to select the most promising molecule for usage in NLO applications. All the calculations are performed in APF-D hybrid functional having dispersion functions and NLO-V basis set.

Computational details

Computational analysis of different 1-naphthol derivatives presented in Fig. 1 was performed in Gaussian 16.A03 [20] package using APF-D [4] functional—which is similar to B3LYP hybrid functional, however is improved through dispersion treatment—and NLO-V basis set [47], dedicated especially for NLO calculations. All the calculations were made both for neutral and ionic forms of each molecule in vacuum to avoid any influence from a medium in which a molecule could be put. In the calculations, the highest possible symmetry of each molecule is considered—the presence of imaginary frequency disqualifies proposed symmetry and the lower point group is then considered. Hence, for naphthalene (N) D_{2h} point group is analyzed, for 1-naphthol (1N) and all its aldehyde derivatives (nA1N) (the exceptions are compounds with the position of 6 and 8— C_1 point group) C_s point group is considered, for all thio (nSH1N) and ester (nE1N) derivatives of 1-naphthol the C_1 point group is proposed. The reactivity descriptors were calculated on the basis of natural bond orbital population analysis for optimized structures using the same calculation method as in the optimization process, using the NBO 3.1 program [22].

Global hardness (η) and global softness (S) were calculated (and analyzed) as it was indicated in [46, 60, 61, 66]:

$$\eta = \frac{I - A}{2} \quad (1)$$

$$S = \frac{1}{\eta} \quad (2)$$

where I is the ionization potential and A is the electron affinity.

Fig. 1 The schematic figure of all studied bi-substituted molecules; R with number denotes the substituent is attached in the position indicated with the number, e.g., for the 4E1N the n is equal to 4 and R4 stands for OCOCH_3 in the position 4 of the ring; in all the positions, except the specific n, there are hydrogen atoms

I and A descriptors (their definitions can be found in [28, 39] respectively) were calculated from the energies of neutral and ionic forms of each studied molecule instead of simplified calculations based on HOMO-LUMO energies due to the fact that for almost all of the commonly used exchange-correlation functionals, the negative of the HOMO energy is not close to the exact ionization potential and can be used only to semiquantitatively estimate the ionization potential, electron affinity, electronegativity, hardness, and first excitation energy [67].

Electronegativity (χ) and electrophilicity (ω) (according to information shown in [48, 57, 61]) were calculated using the formulas presented in [12]:

$$\chi = \frac{I + A}{2} \quad (3)$$

$$\omega = \frac{\chi^2}{2\eta} \quad (4)$$

In the case of local reactivity descriptors, for each atom in the molecule, two different basic reactivity indexes were used: Fukui functions and local softness.

It was showed [21, 26] that the greatest values of the Fukui functions are associated with the greatest reactivity sites of the molecule. To predict the behavior of the molecule for electrophilic attack, it is necessary to use f^- Fukui function, for nucleophilic attack one needs to use f^+ Fukui function [21], while for the radical attack the f^0

Fukui function should be used [37]. The Fukui functions were calculated using the following formulas [16]:

$$f_k^+ = q_k(N+1) - q_k(N) \quad (5)$$

$$f_k^- = q_k(N) - q_k(N-1) \quad (6)$$

$$f_k^0 = \frac{q_k(N+1) - q_k(N-1)}{2} \quad (7)$$

where N is the number of electrons in ground-state geometry of neutral system [37]; q_k is the charge on k -th atom.

Additionally, a dual descriptor, Δf_k , was calculated as the index of selectivity toward both nucleophilic and electrophilic attacks. It is defined as in [41]:

$$\Delta f_k = f_k^+ - f_k^- \quad (8)$$

If $\Delta f_k > 0$, then the site is favored for a nucleophilic attack, whereas if $\Delta f_k < 0$, then the site could be favored for an electrophilic attack [41].

To obtain relative electrophilicity (s_k^+/s_k^- ; to facilitate the notation, the subscripts in all local descriptors will be omitted, thereby it will be written as s^+/s^-) and nucleophilicity (s_k^-/s_k^+) (further written as s^-/s^+) descriptors, the local softness has to be calculated. The local softness will not be studied here itself because of the well-known fact that the local softness contains the same information as the Fukui functions [51]. The formulas for s_k^+ , s_k^- are calculated, multiplying appropriate Fukui functions per global softness [51].

Additionally, in the similar way as in the case of Fukui functions (see Eq. 8), the Δs_k was calculated as in [41]:

$$\Delta s_k = S(f_k^+ - f_k^-) = s_k^+ - s_k^- \quad (9)$$

In the case of NLO properties, the dipole moments (μ), polarizability (α), and first- (β) and second- (γ) order hyperpolarizability tensors were considered. The nonlinear optical properties were analyzed for the static and dynamic, 532-nm wavelength, cases. The obtained values were calculated according to the following formulas [10, 24]:

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (10)$$

$$\beta = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (11)$$

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \quad (12)$$

$$\beta_y = \beta_{yyy} + \beta_{xyy} + \beta_{yzz} \quad (13)$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz} \quad (14)$$

$$\gamma = \frac{\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})}{5} \quad (15)$$

The calculated values are then compared with reference material. The urea molecule is used as the fundamental NLO

reference material [31]. The comparison could be done due to the asseveration of the same conditions of calculations. The urea molecule symmetry was chosen as C_2 as the most stable [56].

Results and discussion

As the basis of further work, it is necessary to study structural properties of isomeric molecules differing in substituent place in the naphthalene ring and their potential of usage in relation to certain properties. For this aim, two representatives of different electron-directing groups were chosen both exhibiting moderate electron directing effect to analyze its average influence on the properties of the molecules. As EWG the aldehyde group and as EDG the thio and ester groups were chosen (as it is presented in Fig. 1). The choice of two EDGs was dictated by some problems with geometry optimization of the thio derivatives in positions 2, 3, 7, and 8. We assumed the electrons from the thio group are too close to the hydroxyl group and their repulsion is the case of a problem with the geometry optimization procedure. Hence, a little more extensive substituent was studied—the substituent from the simplest ester: as the R group, the methyl group was chosen.

Optimized structures

All studied molecules' geometries were optimized for the highest possible symmetry of each molecule at the ground state. In Table S1 in Supplementary Information (SI), there are structural parameters associated with aromatic ring bond lengths and valence angles and the values of the bonds between the aromatic carbon atom and oxygen atom from hydroxyl group (C-O) and between the aromatic carbon atom and first atom of the substituent (C-subst), in relation to corresponding parameters of naphthalene ring (N compound) and unsubstituted 1-naphthol molecule (1N compound).

As it can be seen from Table S1, deviations from N/1N molecules for all the compounds are quite small, differing less than 0.035 Å in the case of maximal deviations and 0.002 Å in the case of average deviations. Greater deviations are observed for the angles: while average deviations are 0.36/0.35° in relation to N/1N molecules respectively, the maximal deviations are 4.5°. As expected, better geometry accordance is found in relation to 1N molecule than N. Among all studied compounds, 3A1N and 5E1N have the geometric parameters the most similar to unsubstituted molecules; on the other hand, thio compounds have the least similar geometry, which could be taken as the confirmation of strong repulsion between both substituents distorting the shape of the naphthalene ring.

It is known for the naphthalene case that EDG directs new substituent to the same benzene ring (having 1–4, 9–10 positions numeration, as shown in Fig. 1) of naphthalene whereas EWG causes substitution in the other benzene ring (atoms with numbers 5–10), thereby for hydroxyl group, which is highly EDG, and another EDG (like ester substituent), the most probable positions for bonds are 2 and 4 (very similar probability of both positions) due to the *ortho*- and *para*- substitution—the effect is enhanced by the presence of two EDG groups—the positions indicated by EWG are the least probable; hence, the bonds formed there (positions 6 and 8) are the weakest (longest). Here, positions 3 and 7 are similarly probable due to the same, quite small, distance from the OH group and are comparably influenced by its presence. For the position 5, electron charges are dispersed almost symmetrically (some differences could result from substituent type and its directing effect magnitude): as a result, the bond formed here should not be strong.

A quite different situation is observed when EWG is used as the second substituent group. We assume there is a possibility of some influence from the interaction between partially negative-charged OH group and partially positive-charged EWG. Due to the high magnitude of the EDG effect, the influence of the hydroxyl group would be greater than the EWG group, and the observed order of bond lengths is similar to the case of both EDG groups (the extreme positions: 8, 5, 2). The lengths of the other bonds are reversed in relation to the case of the two EDGs.

A more detailed description can be found in Supplementary Information (SI).

Energy

In Table S2, there are presented energetic relations presented between all studied molecules differing in substituent position.

For studied EWG, the most stable is the compound with the substituent at position 3 (what is shown in Fig. 2). However, the following three energetically stable compounds (2A1N, 6A1N, 7A1N) should be almost equally probable at room temperature because the energy difference is less than 1 kcal/mol. The least energetic stable is 8A1N (more than 6 kcal/mol in relation to the 3A1N). The energy order of the compounds is as follows:

The high energy of compound having the substituent at the position 8 is obvious; in its geometry, the substituent is partially perpendicular to the plane of the 1-naphthol (as can be seen in Fig. S1), which is highly energetically non-preferable (the same type of geometry is observed for 6E1N molecule). The rest of the molecules is ordered symmetrically (the substituent positions 5 and 4, 7 and 2,

6 and 3) and the structure, in which both substituents are localized at the same benzene ring, has lower energy.

The energy of the compound having two EDG groups (OH and ester groups) is the lowest for 2E1N (see Fig. 2) and 7E1N. The molecules could probably form O-H-O interaction between the hydroxyl group and oxygen atom from the ester group, which significantly minimizes energy (for 7E1N the formation of interaction is more difficult due to the necessity of engaging almost the whole molecule) in relation to the other molecules with the substituent (the energies are greater than 11 kcal/mol in relation to 2E1N). The highest energy is found for 6E1N due to its geometry (as it was analyzed previously, see Fig. S1). Here, also the order of the molecules due to their symmetrical relations (as in the case of the EWG substituent) is preserved; thereby, 3E1N is the second-highest energy molecule. Then, molecules having perpendicular substituent orientation (8E1N and 5E1N) are next. As in the case of EWG, among symmetric positions, energetically preferred are the positions in which both substituents are present in the same benzene ring. Only two pairs (5E1N-8E1N and 3E1N-6E1N) have comparable energies and could be present at equilibrium at room temperature. The energy sequence of the compounds is as follows:

$$6E > 3E > 8E > 5E > 4E > 7E > 2E$$

IR spectra

The infrared spectra of all studied 1-naphthol derivatives are simulated. Additionally, the analysis of IR frequencies having intensities more than $5 \text{ M}^{-1}\text{cm}^{-1}$ was performed using the GaussView program. Due to the lack of scaling factors for the method and basis set and any experimental spectra (to scale the calculated values to the most intense peaks), the presented values are shown as pure data from

Fig. 2 Analysis of relative energetic relations between different 1-naphthol derivatives for studied EWG and EDG in relation to substituent position in naphthalene ring

calculations. For all the simulated spectra (Fig. S2), there is performed a detailed analysis of vibrations divided into the aromatic ring and substituent vibrations (Table S3) and type of modes (Table S4). Additionally, there are presented the vibrations of the SH group which improve the knowledge about more complex organic molecules with thio substituents (than simply thiol-substituted aliphatic hydrocarbons [40]) not studied theoretically in detail yet.

The exemplary IR spectrum for 6E1N is presented in Fig. 3. The vibrations of the OH group are localized near 3750 and 250 cm^{-1} (for ester substituents there is an additional OH peak around 1250 cm^{-1}). The vibrations of the substituent can be analyzed as C-H vibrations, C-O vibrations, and SH vibrations. For both substituents having C, H, and O atoms, the vibrations of C-H can be found near 1500 and 3000 cm^{-1} (for nE1N molecules, there are additional peaks as shown in Tables S3 and S4) and for C-O, the vibrations around 1915 cm^{-1} . The vibrations of the SH group are found at about 1300 , 2300 , and 6780 cm^{-1} . All the values are in accordance with experimental data: OH around 3610 cm^{-1} , phenolic C-O around 1260 cm^{-1} , C-H in methyl group around 3000 cm^{-1} , C-C benzene ring vibrations in the ranges: 1585 – 1600 and 1400 – 1500 cm^{-1} [3] and SH vibrations in the range greater than 5000 cm^{-1} [40].

Selected property analysis

Reactivity

Reactivity has a crucial role in chemistry because of its association with reaction mechanisms, thereby it allows understanding and describing chemical reactions that is a very important task in improving synthesis procedures to obtain new materials [7]. In Table 1, the global reactivity descriptors are presented; and in Table 2, the selected local reactivity descriptors are listed. More detailed data can be found in Tables S5, S6 (the global reactivity descriptors of

Fig. 3 Simulated IR spectrum of 6E1N molecule

Table 1 The selected reactivity descriptors calculated from the energies of neutral and ionic forms of each molecule; values expressed in eV (only in the case of S the values are in eV⁻¹); for more details, see “Computational details” section

Compound	HOMO	LUMO	Δ	I	A	η	χ	ω	S
N	-6.74788	-1.72221	5.026	8.520	-0.019	4.269	4.251	2.116	0.234
1N	-6.13372	-1.40955	4.724	7.897	-0.312	4.105	3.792	1.752	0.244
4A1N	-6.38815	-1.95242	4.436	8.069	0.308	3.880	4.188	2.260	0.258
5A1N	-6.33998	-2.12875	4.211	8.048	0.463	3.792	4.256	2.388	0.264
4SH1N	-6.09971	-1.67568	4.424	7.801	0.016	3.893	3.908	1.962	0.257
5SH1N	-6.18706	-1.64357	4.543	7.873	-0.010	3.942	3.932	1.961	0.254
4E1N	-6.23576	-1.58806	4.648	7.879	-0.018	3.948	3.931	1.957	0.253
5E1N	-6.30951	-1.68330	4.626	7.975	0.054	3.961	4.014	2.034	0.252

all studied molecules and the analysis of the reactivity order for each studied substituent position), **S7** (the list of atoms, for which f^+ Fukui functions are dominating), **S8** (the list of atoms, for which f^- Fukui functions are dominating), **S9** (the list of atoms, for which s^+/s^- electrophilicity descriptor has major influence), **S10** (the list of atoms, for which s^-/s^+ nucleophilicity descriptor is dominating), and **S11** (the analysis of Δf and Δs dual descriptors) in **Supplementary Information**, as well as a more detailed description of the reactivity of naphthalene and 1-naphthol molecules.

Frontier orbitals The most important orbitals in a molecule are labeled the frontier orbitals: HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital). The orbitals are strictly associated with molecule ability to donate (HOMO) and accept (LUMO) an electron; thereby, the frontier orbitals are directly related to ionization potential and electron affinity respectively [57].

The energy band gap associated with energy charge transport is calculated in the form of the energy difference between HOMO and LUMO orbitals as the analogs of the valence and conduction bands, respectively [17]. The HOMO-LUMO energy gap is generally the electronic excitation energy in a molecule having possibly the lowest energy [63]. It is obvious the large value of the HOMO-LUMO energy gap implies high kinetic stability and low chemical reactivity [2] due to the hindered electron possibility to transfer to LUMO level from distant HOMO level. It was found in [17] that the band gap energy decreases progressively with the number of benzene rings (the experimental data of E_{gap} (eV) was derived for a few aromatic hydrocarbons: naphthalene (4.14), anthracene (3.20), tetracene (2.54), and rubrene (2.20)). Values calculated for the naphthalene confirmed it is a very stable compound [2].

According to data collected in Tables 1 and S5, the obtained values of E_{gap} are in the range between 4.21 (5A1N) and 5.03 (N) eV which indicates tested compounds

Table 2 The most reactive places of studied compounds using different local descriptors: Fukui functions (f^+ , f^- , f^0), relative electrophilicity (s^+/s^-) and nucleophilicity (s^-/s^+), Δf and Δs dual descriptors; the atom numeration in accordance with Fig. 1; in ester substituent carbon atoms are numbered as E1 (carboxyl substituent) and E2 (methyl substituent); hydrogen atoms are listed as H-carbon atom number, e.g., H7 means hydrogen atom associated with C7 of the naphthalene ring

Compound	f^+	f^-	f^0	$\frac{s^+}{s^-}$	$\frac{s^-}{s^+}$	Δf	Δs
N	2, 3, 6, 7	H1, H4, H5, H8	9, 10	9, 10	1, 4, 5, 8	2, 3, 6, 7	2, 3, 6, 7
1N	2	H ^{OH}	10	1	5	2	2
2A1N	7	H ^{OH}	10	O ^{CHO}	8	4	4
3A1N	2	H ^{OH}	10	1	4	2	2
4A1N	2	H ^{OH}	10	1	O ^{CHO}	2	2
5A1N	2	H ^{OH}	10	1	6	2	2
6A1N	7	H ^{OH}	10	1	6	O ^{OH}	O ^{OH}
7A1N	2	H ^{OH}	9	1	5	2	2
8A1N	O ^{OH}	H ^{OH}	10	1	O ^{CHO}	2	2
2E1N	E2	E1	10	6	O ^{E1}	E2	E2
3E1N	E2	E1	10	1	4	E2	E2
4E1N	E2	E1	10	1	4	E2	E2
5E1N	E2	E1	10	1	4	E2	E2
6E1N	E2	E1	10	1	8	E2	E2
7E1N	E2	E1	9	1	5	E2	E2
8E1N	E2	H ^{OH}	10	1	5	E2	E2

can be classified as hard molecules due to the large values of energy gap [19]. It is clearly seen among studied compounds that the most symmetric and aromatic molecule—naphthalene—has the highest value of band gap; the presence of the single substituent (OH group) in 1N causes a drop in the value of band gap confirming the substituent influence on π -electron delocalization in the aromatic ring (the influence is weak [27], about 0.3 eV) and greater reactivity of 1-naphthol over naphthalene [9]. All tested 1-naphthol derivatives should exhibit high stability. However, for the same substitution position, higher values of E_{gap} have molecules with EDG rather than EWG, as presented in Table 4 and Fig. 4. Especially high differences of reactivity are found for the *ortho* and *para* positions in the second benzene ring, whereas E_{gap} for the position 4 is not influenced by the type of electron-directing group and is the most stable position in the ring. The order of stability is as follows:

HOMO orbital is related to the sites of prospective electrophilic attack and LUMO is linked with the nucleophilic attack site [26]. In Fig. 5, the exemplary HOMO and LUMO orbitals are presented (the frontier orbitals of N, 1N, and all tested 1N derivatives are shown in Fig. S1a). The positive phases are the red regions whereas the negative phases are green regions [63].

Despite the type of tested derivatives, the HOMO orbital is localized in the region of the carbonyl group of the substituent, with the main influence from the carbonylic oxygen atom, and the LUMO orbital is localized mainly in the region of the C1, C2 atoms with small influence from surrounding (C3 and C9) atoms. When there is no carbonyl substituent (as in the case of 1N and thio derivatives),

Fig. 4 The analysis of E_{gap} of studied compounds in relation to a substituent position; the 5A1N (as having the minimal value) is used as the reference

the HOMO orbital has the same localization as in the unsubstituted naphthalene molecule.

MEP Molecular electrostatic potential (MEP) surface is used to visualize variable charged regions of a molecule with colors associated with different electrostatic potential values: red (represents the regions of most electronegative electrostatic potential—electron-rich places [55]), blue (as the most positive electrostatic potential—electron-deficient places), and green (as zero potential—neutral places). The potential decreases in the order: blue > green > yellow > orange > red [57]. MEP can be useful to analyze the polarization and charge transfer effects within molecules [55], their molecular structures, physico-chemical property relationships, and the interactions between studied molecules by showing the shape, size, charge density, and site of chemical reactivity of the molecules [57].

The addition of the EWG group generally causes charge transfer from the hydroxyl group through the naphthalene ring to the aldehyde group (as can be seen in Fig. S1b). When both substituents are attached to the same benzene ring (2A1N, 3A1N, and 4A1N), the charge transfer is smaller than in the case in which electrons have to flow through both benzene rings (5A1N, 6A1N, 7A1N, and 8A1N) to find oxygen atom from the CHO group. The least reactive structure is 4A1N in which substituents are in the *para* position in relation to the benzene ring—the electrons are scattered within the almost whole molecule. On the other hand, the most reactive structure is 8A1N—the electrons move through all the molecules to accumulate at the oxygen atom of the aldehyde group. The reactivity of the 1-naphthols with aldehyde group in the second benzene ring is as follows: 5A1N < 6A1N < 7A1N < 8A1N, which is indicated by increasing electron-rich character (yellow color of MEP) of the region near the oxygen atom from the aldehyde group. The situation in 5A1N and 6A1N is quite similar to 1-naphthols with both substituents in the same benzene ring (see 2A1N and 3A1N in Fig. S1b) with a slightly greater electronegative potential of the aromatic ring; in 6A1N, the contribution of electron-rich regions near the oxygen atom is greater than that in 5A1N. The most reactive are 7A1N and 8A1N molecules in which there is a possibility of forming O–H–O weak interactions (as it is presented by the example of 7E1N in Fig. 6; the analogous situations can be observed in 2E1N, 3E1N, and 7E1N molecules) stronger in 8A1N due to the proximity of both oppositely charged substituents separating charges (in 8A1N the contribution of yellow—as slightly electronegative place indicator—is the greatest among all nA1N molecules and is deployed continuously from the aromatic ring to the oxygen atom of aldehyde group).

The presence of the second EDG group (ester substituent) usually has a similar influence as the addition of

Fig. 5 The frontier orbitals of naphthalene and selected 1-naphthol derivatives calculated with NBO method

EWG: here, the charge transfer follows from the hydroxyl group to the oxygen atom of the second substituent. The only difference is made by the place of substitution resulting in the reactivity of the structure (the comparison of both substituents and their MEPs is presented in Fig. S1b). The most reactive is the 2E1N molecule: the nucleophilic center is localized on the methyl group and the naphthalene ring is the most electronegatively charged region. On the other hand, the least reactive is the 5E1N molecule: the situation is very similar to 4A1N. The reactivity order for both types of groups (based on the results shown in Table 1) is presented below:

for the EWG and EDG groups respectively. It can be summarized that, firstly, the addition of the EWG substituent causes an increase of reactivity in relation to EDG

substituents and, secondly, the highest reactivity is observed for molecules for which there is a possibility of O–H–O weak interactions formation (as in 7A1N, 8A1N and 2E1N, 3E1N, 7E1N molecules).

Global reactivity descriptors The global reactivity descriptors like ionization energy, electron affinity, global hardness and softness, and electronegativity and electrophilicity index describe the properties of a molecule as a whole [60].

Their detailed analysis as well as some useful definitions can be found in SI.

One look at the overview of the global reactivity descriptors will show that the order of molecules when ordered according to different global reactivity descriptor is inconsistent, e.g., for η the most reactive is a molecule with a substituent in the position 8 (for both tested types of electron-directing groups) while for ω the most reactive are 5A1N/6E1N molecules (see page A17 in SI). However, the observed situation is not unique. In literature, there are cases, in which the order of reactivity according to different descriptors is generally consistent (e.g., μ , χ , S , ω in Table 4 in [7]), but the vast majority of papers also reports different sequences of reactivity of studied molecules, which depends on tested descriptors (like in [12, 38, 53, 55, 64, 67]). More detailed research shows that both variants are natural—it was shown in [46] the reactivity order based on global reactivity descriptors obtained from experimental values for atoms could be very similar during the analysis of certain parameters set, e.g., χ , η for Li, Na, Al atoms shown in Table 1 in [46] or differs significantly when another set of parameters is chosen (e.g., I , A , χ for Li, Na, Al).

After summarizing all the descriptors of global reactivity (see Table 1; full data is presented in the Table S6),

Fig. 6 The molecular electrostatic potential (MEP) calculated for 7E1N molecule

it was found that the most reactive are structures with EWG when charges are transferred through the whole molecule and accumulated in the second benzene ring, whereas the least reactive when charges are accumulated near each other in the same benzene ring as the hydroxyl group. For EDG structures, there is no such tendency to be found. It can be generalized that the most reactive molecules have substituents in the position 7 (and 5/2 for EWG/EDG respectively) whereas the least reactive ones are the molecules with substituents attached to the first benzene ring (with hydroxyl group)/second benzene ring (2A1N, 3A1N, 4A1N and 8A1N/4E1N, 5E1N, 6E1N, and 8E1N) for EWG/EDG respectively.

It is showed from the table that the order of the most reactive molecules is as follows:

And the order of the least reactive molecules:

The substituent in position 4 regardless of the electron-directing group is found to be the most nucleophilic center. For 1-naphthol derivatives with EWG, the most electrophilic are substituents in the positions 5 and 7 (*ortho* and *para* positions in the second benzene ring), whereas for EDG substituents with the *meta* positions 3 and 6.

Local reactivity descriptors While global descriptors are related to the reactivity of chemical systems, local descriptors are related to the concept of selectivity. The key concepts in selectivity are the Fukui functions and the local softness. Unfortunately, the descriptors are not always able to identify unequivocally the specific sites where a reaction is favored or cannot take place [41]. Thereby, as the local reactivity descriptors, both the Fukui functions [66] and local softness were chosen as well as the descriptors derived from them: relative electrophilicity s^+/s^- and relative nucleophilicity s^-/s^+ [51], Δf_k and Δs_k dual descriptors.

Due to the fact Fukui functions (and as the consequence the relative electrophilicity and relative nucleophilicity descriptors) are determined based on atom charges calculated using population analysis, the accuracy of the values of the local descriptors will depend not only on the accuracy of the calculation method but also on the selection of proper population analysis [26]. All the calculations were performed using NBO population analysis as giving realistic charge distribution [33].

Our results (presented in the Tables 2, S7, and S8 and as a more detailed description of each type of Fukui function

in SI) indicate there is no similarity of reactive sites among tested local descriptors even though within the molecule the relative values of the Fukui function and local softness provide the same information. It means that the place, where the Fukui function is large, is very soft, whereas small values of the Fukui function imply hard regions [37].

The calculated values of different local descriptors are usually in no accordance, which was illustrated in Table 2. However, the situation is not unique. It was shown in [37] that it can happen that although the softest atom is, in general, the most reactive site of the molecule, there may be the other sites with smaller values of softness, that may become the most reactive sites, depending on the softness of the reacting molecule of the nucleophile/electrophile.

The picture of reactivity formed with Fukui functions is consistent with the expectations: when an electron is taken from the system, the most reactive are electron-rich places: hydrogen atoms, H^{OH} ; when an electron is added to the molecule, the atom reactivity is focused on O^{OH} and carbon atoms in the *ortho* positions in relation to the hydroxyl group to replenish partly positive charges on the atoms resulting from the EDG effect of the hydroxyl group.

The analysis of the relative electrophilicity and nucleophilicity is based on the following condition: the site having the highest s_k^+/s_k^- is the most probable site to be attacked by a nucleophile, and the site having the highest s_k^-/s_k^+ ratio is the most probable site to be attacked by an electrophile [51].

The trend obtained from the results of s_k^+/s_k^- and s_k^-/s_k^+ (shown in Tables 2, S9, S10 and their analysis performed in SI) seems to be acceptable; however, the high reactivity of the positions 9 and 10 (as it is presented in Table 2) is not much trustworthy from the chemical point of view. The places are not reactive in the naphthalene ring; hence, the only explanation of the results could be the high mobility of electrons, which are instantaneously transferred from the places to the neighboring atoms due to the steric hindrance of carbon atoms forming naphthalene ring.

The analysis of dual descriptors Δf and Δs (for the calculation method, see Eqs. 8 and 9) is quite simple due to the order of atoms in substituted naphthols, arranged from the most electrophilic to the most nucleophilic. The results (presented in the Tables 2, S11 and the corresponding detailed description in SI) are very similar—there are only small differences in the order of atoms, not affecting the general picture of reactivity, thereby both descriptors will be analyzed at the same time (full analysis data is presented in Table S11).

The results are in good accordance with Fukui functions, thereby both the dual descriptors as well as Fukui functions can be used to predict the reactivity of a molecule which is consistent with the chemical expectations. Our calculations cannot confirm results presented in [50] that softness (and

Fig. 7 The analysis of studied local descriptors for both tested types of electron-directing groups: for each pair on the left is EWG and on the right is EDG. The position of substituents is arbitrary and shown

for a 5-substituted 1-naphthol molecule. The electrophilic/nucleophilic center is presented as +/– in a circle respectively

not Fukui functions) should be a better descriptor of the reactivity.

The picture obtained from all local descriptors calculations is coherent and it predicts that the derivatives with EWG have structures (as it can be seen in Fig. 7), in which both substituents affect the polarity of the molecule. Following the concept of electron donation as the crucial mechanism for anti-corrosion properties [42], it is clear that the 1-naphthol derivatives with EWG substituents can inhibit corrosion due to the ability of such system to donate electrons (to neutralize radical species) and at the same time the presence of delocalized electrons from naphthalene ring stabilizes the molecule. Additionally, the second substituent (hydroxyl group) can behave as a shield protecting the system against electrons from the external medium.

As it is seen from Fig. 7 and data in Table 2, the substituted 1-naphthols may be anti-corrosion useful even in the case of surfaces with electron excess. The additional functionality of such structures is that they have also electrophilic centers so it is a way to bond them to the surface of interest and decrease its reactivity.

NLO properties

The values of dipole moments, static and dynamic polarizability, and first and second-order hyperpolarizability tensors for tested compounds are listed in Table 3 (full data is collected in Table S12 as well as more detailed analysis of the NLO properties presented in SI).

Generally, the best positions for high polarization (indicated by dipole moment values) are 5 and 6 providing a large distance between both substituents, whereas for low polarization good choice is position 2 (two neighboring positions in the same benzene ring).

In the matter of the thio derivatives, the values are extremely high for the compounds having a substituent in the positions 4 and 5 (more than 44 Debye, which is 25 % more than calculated for single DAST molecule [45]) and quite big for the position 6 of the aromatic ring.

The values of static and dynamic NLO properties are comparable and the dynamic ones are always slightly larger (the exception are thiol derivatives). Thereby, the analysis will be performed for the static case. The visual overview

Table 3 The NLO parameters of selected molecules; the dipole moment expressed in Debye, the polarizability and hyperpolarizability tensors in ESU units; values for α , β , and γ should be multiplied by 10^{-24} , 10^{-30} , and 10^{-36} respectively

Compound	μ	μ_x	μ_y	μ_z	Static			Dynamic for 532 nm		
					α	β	γ	α	β	γ
N	0.000	0.000	0.000	0.000	15.894	0.000	1.814	16.930	0.000	2.741
1N	1.610	−1.357	0.866	0.000	16.697	1.248	2.125	17.891	2.148	3.547
3A1N	1.806	−0.243	1.789	0.000	19.499	4.143	6.920	21.263	8.226	16.063
6A1N	3.488	1.560	3.119	0.000	19.494	5.718	7.554	21.211	12.433	20.812
7A1N	2.514	−0.807	2.381	0.000	19.477	5.774	7.294	21.278	12.663	17.276
8A1N	2.126	1.863	−0.977	0.307	18.839	1.159	3.636	20.309	2.885	7.660
2E1N	2.230	−1.302	1.810	0.000	22.303	2.989	7.161	24.201	4.266	13.223
5E1N	3.974	−3.481	−0.031	1.916	20.868	0.850	3.498	22.272	1.869	6.556
7E1N	1.078	−1.010	0.375	0.000	22.262	4.398	10.338	24.081	9.067	20.362
8E1N	2.583	−1.598	−1.180	1.651	20.806	1.969	3.227	22.176	3.277	5.957

of the NLO activity of each position in the aromatic ring is presented in Fig. 8.

In all the cases, structures having substituents at positions 5 and 8 lead to the least NLO active molecules while the positions 7 (both types) and 3,6/2,4 (EWG/EDG respectively) lead to the most NLO active compounds.

The values of α for EWG are maximally 17% greater than in unsubstituted 1N, whereas for EDG is 34% respectively. It is worth to note that the smallest value for EDG is about 7% bigger than the greatest value for EWG. For both groups, the maximal values are obtained when the substituent is in the same benzene ring as the hydroxyl group while the minimal values are found for the substituent in the second benzene ring at the same position as the OH group.

While alpha values are at a comparable level, beta values are strictly associated with the position and type of

Fig. 8 Correlation between the substitution position and the value of the polarizability and hyperpolarizability tensors

Table 4 The calculated lowest (on the left) and highest (on the right) values of tested NLO properties for each group having a moderate magnitude of electron-directing effect in relation to the urea molecule (the values for the urea are taken as 100%)

	EWG		EDG	
μ	−33 %	+32 %	−61 %	+45 %
α	+414 %	+432 %	+468 %	+509 %
β	+555 %	+3162 %	+380 %	+2385 %
γ	+2231 %	+4742 %	+1969 %	+6527 %

substituent. For EWG, the values are more than 2.4 times bigger than in 1N (the exception is the 8A1N molecule, whose value is slightly less than in 1N). For EDG, the values are also greater than in 1N (with the exception for 5E1N), but smaller than for EWG.

Gamma value increases with the presence of additional substituents: the addition of OH group increases its NLO behavior more than 15%, and further substitution improves the second-order hyperpolarizability value more than 70/50% for EWG/EDG groups respectively. The maximal and minimal values of gamma can be found, as in the case of beta, for the second benzene ring positions.

Generally, among all tested monosubstituted 1-naphthol derivatives, there is no one position giving the best results of all NLO properties. Analysis for each position shows that for almost all positions the finest values are obtained for the EDG, the exceptions are positions 4 and 7. The comparison with values calculated using the same method for the urea molecule having C_2 point group symmetry presented in Table 4 shows more than 5/6 times larger values of alpha, 32/24 times larger values of beta, and 48/66 times larger values of gamma for EWG/EDG respectively. For 532 nm (dynamic case), the results are enhanced even more: α 6/7, β 61/144, γ 119/116 times larger (EWG/EDG) when referring to the urea molecule.

Conclusions

In summary, the detailed theoretical analysis concerning 1-naphthol derivatives differing in substituent type and its position in the naphthalene ring was performed.

Calculations with APF-D/NLO-V method showed the thio derivatives of 1-naphthol can exist only for the positions 4, 5, and 6 of the aromatic ring; the other structures are not possible due to the strong repulsion of electrons from both substituents. According to expectations, electron-directing groups have a substantial contribution to the obtained geometry (bond lengths, valence angles). EDG has a crucial influence on the stability of molecules (energetic relations and E_{gap}); it was found that more stable are molecules having a substituent in the same benzene ring

as the hydroxyl group; for the same substituent position, higher values of E_{gap} are given by EDG rather than EWG. Calculations reveal that for the molecules with substituents in positions 7 and 8 (and 2E1N), there is a possibility of forming intramolecular O-H-O interactions, which was indicated by energetic relations between isomers, MEP, and global reactivity descriptors.

The IR spectra were simulated for all studied compounds and the vibrations are in accordance with the literature.

The most reactive structures with EWG are molecules in which charges are transferred through the whole molecule and accumulated in the second benzene ring, whereas the least reactive when charges are accumulated near each other in the same benzene ring as the hydroxyl group. For EDG structures, there is no such tendency to be found. The most reactive molecules have substituents in position 7 (and 5/2 for EWG/EDG respectively), whereas the least reactive are molecules with substituents attached to the first benzene ring (with hydroxyl group)/second benzene ring for EWG/EDG respectively. Global reactivity descriptors analysis confirm that conclusion: it is seen the least reactive are molecules with the possibility of more regular electron distribution occurrence when EDG is a substituent whereas for EWG as a substituent when the substituents are localized as close as it is possible. The study of local reactivity descriptors showed that all the tested compounds do not exhibit radical character; the carbon atoms of naphthalene and oxygen atoms are nucleophilic sites, whereas hydrogen atoms and C1 carbon atom are electrophilic ones. The picture of reactivity generally (the exception is s^+/s^- and s^-/s^+) is consistent with expectations.

1-Naphthol derivatives having EWG as substituent could be effective low-cost anti-corrosion materials. The high stability of the aromatic structure coupled with the polarity of the molecule provided by a different type of substituents allows for permanent connection with a surface to be protected and the reduction of its reactivity.

The addition of the second substituent to 1-naphthol improves the NLO properties. The most NLO active are molecules with a substituent in position 7, the least in the positions 5 and 8. Greater values of polarizability tensors are observed for almost all positions of naphthalene ring for compounds having EDG in comparison to molecules with EWG; the first-order hyperpolarizability tensor values are bigger when EWG is used as the substituent.

The hyperpolarizability tensors obtained for all substituted naphthols are much greater than in the urea molecule—they are even sixty times greater for the static case; for the dynamic case, values of hyperpolarizability tensors for some substituents are over a hundred times greater.

It means that substituted naphthols may be considered as very good materials for NLO devices and anti-corrosion protection. They are chemically stable and, what

is important from the practical point of view, not expensive. They are also easy to be used in polymer composite preparation; hence, they could be used as effective components of multifunctional material systems.

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Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Author contributions All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Ilona Radkowska (I. Radkowska) and Piotr Bragiel (P. Bragiel). The first draft of the manuscript was written by I. Radkowska and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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