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Experimental and Theoretical Insights into Molecular and Solid-State Properties of Isomeric Bis(salicylaldehydes)

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ABSTRACT: A series of five bis(salicylaldehydes) including four isomeric compounds based on a benzene scaffold and a closely related naphthalene derivative were investigated in order to elucidate the impact of resonance effects and intramolecular hydrogen bonds (HBs) on macroscopic properties of these systems. Density functional theory (DFT) computations revealed important differences between isomers on the molecular level, which reflected in different charge distribution, aromatic C–C bond orders and aromaticity characters. Consequences of these features were evidenced by the UV-Vis absorption spectra: 1,3-diformyl-4,6-dihydroxybenzene **2** longest

wavelength absorption band is observed at 285 nm, while its isomers 1,4-diformyl-2,5-1,4-diformyl-2,3-dihydroxybenzene dihydroxybenzene 1. 3. and 1.2-diformyl-3.6dihydroxybenzene 4 are characterized by absorption in the visible range (379-407 nm). The specificity of 2 results from simultaneous lowering and elevation of HOMO and LUMO energy levels, respectively. We have found that the HOMO/LUMO energy variations follow trends observed in isomeric dihydroxybenzenes (HOMO) and phthalaldehydes (LUMO), and these effects operate separately to some extent. Furthermore, theoretical calculations indicate that UV-Vis spectral properties of bis(salicylaldehydes) are directly transferable to corresponding bis(salicylaldimines) and their boron complexes. Finally, the influence of structural and molecular stabilization effects was analyzed by means of X-ray structural analysis and periodic DFT computations.

Introduction

Comparative studies on a series of similar model systems provide an opportunity to get insight into substantial structural relations and interplay between molecular conformation, electron density distribution, solid-state structure and macroscopic properties of organic compounds. For those reasons, polymorphs, isomeric and isostructural compounds are the subject of many comparative analyses.^{1–6} Such systems usually differ in one particular molecular or structural feature, which decreases the number of possible contributors influencing their micro- and macroscopic properties. Nevertheless, the structure-property relationships are usually not straightforward, because they depend on many, usually closely-related aspects originating from both molecular (molecular mass, electron distribution) and environment effects. It is thus reasonable to inspect relatively simple systems, which possess one distinct molecular feature that can be finely tuned among studied series (strength of hydrogen bonds, steric hindrance of

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substituent, etc.). Following these general considerations, we have decided to focus our attention on hydrogen-bonded isomeric systems possessing two pairs of *ortho*-located hydrogen bonds (HB) donors (hydroxyl groups) and acceptors (formyl groups), namely bis(salicylaldehydes) - the difunctional analogues of salicylaldehyde.

Due to the presence of two reactive groups, salicyladehydes are highly versatile synthons for the preparation of various organic molecules. Examples include Wittig olefination, oxidation, and preparation of Schiff bases such as multidentate salen ligands which are extensively used in coordination chemistry.⁷ A number of related N-salicylideneanilines (SANS) exhibit interesting optical properties and can be used in synthesis of luminescent molecules.⁸⁻¹² Due to reversible proton transfer involving keto-enamine/enol-imine tautomerization, selected systems exhibit thermochromic and photochromic behavior.¹³⁻¹⁶ Salicylaldehydes have also attracted a considerable interest from the structural and theoretical point of view. The presence of an intramolecular resonance-assisted HB is a key factor responsible for their specific physicochemical and spectroscopic features including ESIPT (excited-state induced proton transfer) phenomenon.^{17,18} Approaches to evaluation of aromaticity (or more precisely - quasi-aromaticity) of a six-membered H-bonded ring comprising hydroxyl and formyl groups have also been reported.¹⁹⁻²³ As shown by Gilli, Krygowski, Solà, Simon, Palusiak, Houjou and others, in such systems intramolecular HBs gain additional stabilization due to the resonance effect of π -electrons (Chart 1).^{20,24-26} This is accompanied by elongation of the C=O bond and shortening of the C-OH bond. Furthermore, it results in shortening of the O...O distance and elongation of the OH bond, which can be monitored experimentally by ¹H NMR or IR spectroscopy²⁷ and quantified by theoretical calculations. Thus, the term "resonance-assisted hydrogen bond" (RAHB) coined by Gilli et al. in 1989²⁸ is commonly used to describe the H-bonding situation in various β -ketoenol

and other related systems, although (as pointed by Sanz et. al.) in some particular cases it may also result from the constraints imposed by the σ skeleton.^{29–31} Palusiak demonstrated that RAHB has strong impact on mesomeric effects operating in aromatic hydrocarbons and is sensitive to substituent effects.³²



Chart 1. Resonance assisted hydrogen bonding in salicylaldehydes.

More recently, much attention has been paid to bis(salicylaldehydes), due to their utilization as building units for the construction of bi- and multifunctional materials for catalysis and optoelectronics.^{33–45} They are also extensively used for the construction of thermotropic mesogens exhibiting a rich variety of liquid crystal (LC) phases.^{46–50} Furthermore, they were successfully incorporated into the imine-based porous Covalent Organic Frameworks (COFs) and studied for their potential catalytic and optoelectronic applications.^{51–58}

Despite the importance of bis(salicylaldehydes), their molecular and structural features have not been thoroughly studied and compared yet. The Cambridge structural database (CSD) search gives 279 hits of salicylaldehyde structures including several systems bearing two pairs of salicylaldehyde units. However, they are either based on the naphthalene backbone or salicyladehyde units located in different parts of the molecule, *i.e.*, comprising two different aromatic rings. Naphthalene-based bis(salicyl) aldehydes have already been studied by Houjou et. al.²⁰ In the latter examples the mutual influence of CHO/OH pairs is rather limited. Surprisingly, there are no reports on crystal structures of simple bis(salicylaldehydes) based on benzene ring, namely dihydroxydiformylbenzenes. This has prompted us to examine molecular and structural

features of four isomeric bis(salicylaldehydes) 1-4 (Chart 2). To elucidate the effect of the direct π -conjugation, the series was supplemented by symmetrical bis(salicylaldehyde) based on naphthalene backbone, namely 1,8-dihydroxy-2,7-diformylnaphthalene (5), parent salicylaldehyde (A), and 1-hydroxy-2-naphthaldehyde (B). At this point it is noticeable that compound 5 is isomeric to previously studied by Houjou et. al. naphthalene bis(salicylaldehydes) including 2,7-dihydroxy-1,8-diformyl-, 2,6-dihydroxy-3,7-diformyl- and 2,6-dihydroxy-1,7diformyl- derivatives.²⁰ It is expected that studied series exhibit number of useful features: (a) all molecules are rigid and can be treated as topological quasi-analogues of aromatic systems, namely anthracene (1-2), phenanthrene (3-4) or chrysene (5) aromatics, (b) in all cases formation of strongly favored RAHB is expected, which partially saturates HB donor and reduces the number of possible intermolecular hydrogen interactions in the solid state, (c) the molecules are very similar one to another, that facilitates the rationalization of their differences in macroscopic properties (such as UV-Vis spectra) using relatively simple experimental and theoretical tools.



Chart 2. Bis(salicyladehydes) discussed in this study.

Experimental Section

Synthesis

General Information. Starting dimethoxyphthalaldehydes and 2,3-dihydroxy-1,4diformylbenzene were synthesized according to the literature methods.⁵⁹ Reactions and manipulations involving moisture-sensitive reagents were carried out under an argon atmosphere. ¹H, and ¹³C NMR spectra were recorded on Agilent NMR 400 MHz spectrometer. ¹H and ¹³C chemical shifts were referenced to TMS using known chemical shifts of solvent residual peaks.

Synthesis 1. Α ml round-bottom flask was charged with 2.5of dimethoxyterephthalaldehyde⁵⁹ (0.873 g; 4.5 mmol) and argonated. Then, anhydrous DCM (40 ml) was added, and the resulted solution was cooled with ice-water bath. Then BBr₃ (11.3 ml; 11.3 mmol; 1M solution in hexane) was added. After 5 min cooling bath was removed and stirring was continued at r.t. for 3 h. Then water (50 ml) was added, and the mixture was extracted with DCM (5×100 ml). Combined organic phases were washed with water (100 ml), brine (100 ml), and dried over MgSO₄. The mixture was filtered through a pad of silica gel at Schott filter, and evaporated to obtain 1 (0.70 g; 4.2 mmol; 93%) as yellow crystalline solid, mp. 245 °C (dec.); (Lit: 240 °C⁶⁰) ¹H NMR (400 MHz, DMSO- d_6) δ 10.30 (s br, 2H), 10.295 (s, 2H), 7.22 (s, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 190.2, 152.8, 127.7, 115.1.

Synthesis of 2. Dialdehyde 2 was prepared from 4,6-dimethoxyisophthalaldehyde⁵⁹ by demethylation with AlCl₃ in nitrobenzene (120 °C, 1 h), according to the procedure described by Widiger et. al.⁶¹ Crude product was crystallized from ethanol, mp. 186.5-187.5 °C (Lit. 191 °C)⁶⁰). ¹H NMR (200 MHz, CDCl₃) δ 11.77 (s, 2H), 9.78 (s, 2H), 7.81 (s, 1H), 6.45 (s, 1H). ¹³C NMR (50 MHz, CDCl₃) δ 193.9, 168.5, 142.5, 115.6, 104.5.

Synthesis of 3. Sample 3 was available from our previous project reported by us in lit.⁵⁹ Multistep synthesis of 4

Alkylation of 2,3-dicyanohydroquinone. A 100 ml round-bottomed flask was charged with 2,3-dicyanohydroquinone (5.545 g; 34.63 mmol) and flushed with argon. Then, under argon atmosphere K₂CO₃ (19.15 g; 138.6 mmol), DMF (40 ml), and butyl iodide (15.7 ml; 138.5 mmol) were added. The flask was covered with aluminum foil to protect from light, tightly closed with cap, and mixture was vigorously stirred at 90 °C for 20 h. Then, the mixture was cooled to r.t., poured into aqueous solution of NH₄Cl (100 ml; 10 %), and concd aqueous solution of HCl (10 ml; ca. 37%) was added. The resulted mixture was extracted with DCM (3×150 ml), combined organic phases were washed with aqueous solution of LiCl (150 ml; 1M), water (150 ml), brine (150 ml), and dried over anhydrous MgSO₄. The mixture was filtered, evaporated and dried under vacuum to obtain dinitrile **8** as a cream-colored solid (8.175 g; 30.0 mmol; 87%), mp. 187.5-189.5 °C (Lit. 193 °C^{62,63}). ¹H NMR (400 MHz, CDCl₃) δ 7.14 (s, 2H), 4.03 (t, *J*=6.4 Hz, 4H), 1.86-1.70 (m, 4H), 1.57-1.41 (m, 4H), 0.95 (t, *J*=7.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 155.1, 118.5, 113.1, 105.1, 69.9, 30.9, 19.0, 13.7.

Hydrolysis and reduction of 8. A 250 ml round-bottomed flask was charged with **8** (8.175 g; 30.0 mmol) and aqueous solution of KOH (30 g KOH + 30 g H₂O). The flask was fitted with reflux condenser, and refluxed (bath temp.=170 °C) over 6 h. The mixture was cooled with ice-water bath, and aqueous solution of H₂SO₄ (ca. 100 ml; 20%) was added slowly, until the liquid become acidic (tested with universal indicator). Then water (150 ml) was added, and the mixture was extracted with DCM (3×150 ml). Combined organic phases were washed with water (150 ml), brine (150 ml), and dried over anhydrous MgSO₄. The mixture was filtered, evaporated and dried under vacuum to obtain a yellowish solid, which was used directly for the next step. The solid contained two components, most likely diacid and anhydride, and their relative content varied depending on conditions of the aqueous workup.

A 250 ml round-bottomed flask was charged with yellowish solid from the previous step, and argonated. Then, anhydrous Et₂O (60 ml) was added, the suspension was cooled with ice-water bath, and a solution of LiAlH₄ (60 ml; 60 mmol; 1.0 M in Et₂O) was added dropwise with stirring over 15 min. Then, the flask was fitted with reflux condenser and heated to 40 °C under argon for 3 d. Then, ice-water bath was applied, water (100 ml) was added, and most of the solvent was evaporated. An aqueous solution of HCl (150 ml; 3:1 concd HCl:H₂O) was added, and the resulted mixture was extracted with DCM (3×150 ml). Combined organic phases were washed with aqueous solution of NaOH (3×150 ml; 5%), brine (150 ml), and dried over anhydrous MgSO₄. The mixture was filtered, evaporated and separated with column chromatography (\emptyset 9cm \times 6cm; ca. 200 ml of silica gel; cyclohexane:ethyl acetate $10:1 \rightarrow 1:1$) to obtain diol 9 (6.87 g; 24.33 mmol; 81% over two steps) as a cream-brownish powder, mp. 69.5-74 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.78 (s, 2H), 4.81 (s, 4H), 3.92 (t, J=6.4 Hz, 4H), 2.76 (s, 2H), 1.82-1.67 (m, 4H), 1.55-1.39 (m, 4H), 0.95 (t, *J*=7.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 151.3, 129.6, 112.3, 68.8, 56.7, 31.4, 19.4, 13.8. MS (EI, *m/z*, relative intensity): 282 (M⁺, 52), 264 (3), 208 (42), 179 (7), 166 (6), 152 (54), 134 (100), 123 (18), 106 (14), 95 (11). Elem anal, calcd for $C_{16}H_{26}O_4$: C, 68.06; H, 9.28; found: C, 67.84; H, 9.37.

Swern oxidation-dealkylation of diol 9. A 100 ml Schlenk flask was argonated, charged with oxalyl chloride (2.79 ml; 33.0 mmol) and anhydrous DCM (30 ml), and the mixture was cooled to -78 °C. Then, a solution of DMSO (4.69 ml; 66.0 mmol) in DCM (12 ml) was added dropwise over 5 min. The mixture was stirred for 5 minutes, and a solution of diol **9** (4.25 g; 15.1 mmol) in DCM (18 ml) was added dropwise over 10 min. After 90 minutes triethylamine (20.88 ml; 150 mmol) was added dropwise over 10 min, and after next 5 min cooling bath was removed, and the mixture was stirred at r.t. for 1 h. Then, the mixture was poured into water (150 ml), extracted with

DCM (3×150 ml), and combined organic phases were washed with water (150 ml), brine (150 ml), and dried with anhydrous Na₂SO₄. The mixture was filtered through a Schott filter, evaporated and used for the next step.

Warning! The intermediate tends to easily decompose. We recommend to cleave the etheral function as soon as possible, once the oxidation is finished.

A 100 ml Schlenk flask was argonated, charged with dialdehyde from the previous step and anhydrous DCM (30 ml), and cooled in ice-water bath. Then, BBr₃ (30.0 ml; 30.0 mmol; 1.0 M solution in hexanes) was added dropwise with stirring over 5 min. After next 5 min cooling bath was removed, and stirring was continued for 40 h at r.t. Then, the mixture was poured into aqueous solution of NH₄Cl (150 ml; 10%), and extracted with DCM (3×150 ml). Combined organic phases were washed with water (150 ml), brine (150 ml), and dried over anhydrous MgSO₄. The mixture was filtered through a pad of silica gel at Schott filter, evaporated and separated with column chromatography (\emptyset 6cm × 22cm; ca. 400 ml of silica gel; cyclohexane:DCM 8:1→0:1) to obtain aldehyde **4** (0.843 g; 5.07 mmol; 34% over two steps) as a yellow-orange powder, mp. 153.0-154.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 11.86 (s, 2H), 10.73 (s, 2H), 7.27 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 191.3, 156.9, 129.4, 115.5. MS (EI, *m/z*, relative intensity): 166 (M⁺⁺, 100), 137 (89), 120 (14), 109 (19), 92 (32), 81 (24), 63 (13), 53 (31). Elem anal, calcd for C₈H₆O₄: C, 57.84; H, 3.64; found: C, 57.97; H, 3.74.

The aldehyde **4** is a stable compound and can be crystallized by slow evaporation of concentrated chloroform solution from open glass vial on air.

Structural analysis

X-ray structural measurements and refinement details. The single crystals of samples 1-5 were obtained by slow evaporation of CHCl₃ solutions. All except 4 were measured at 100 K on

SuperNova diffractometer equipped with Atlas detector (Cu- K_{α} radiation, $\lambda = 1.54184$ Å). Crystal structure of **4** was exceptionally measured at 250 K due to the crystal instability presumably resulted from phase transition at lower temperature. Data reduction and analysis were carried out with the CrysAlisPro program.⁶⁴ All structures were solved by direct methods using SHELXS-97⁶⁵ and refined using SHELXL-2014.⁶⁶ All non hydrogen atoms were refined anisotropically. The position of OH hydrogen atoms were refined freely, whereas their ADPs were constrained with $U_{iso}^{H} = 1.5 \cdot U_{eq}^{O}$. All hydrogen atoms were visible on the difference-density maps in the proximity of hydroxyl oxygen atom, whereas no density was detected close to the carbonyl atom pointing that hydrogen atom resides on the hydroxyl oxygen atom (Figure S2-S6, SI). All important crystallographic data including measurement, reduction, structure solution and refinement details are placed in **Table 1**. Crystallographic Information Files (CIFs) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no.: 1938693 (1), 1938694 (2), 1938695 (3), 1938696 (4), 1938697 (5).

Table 1. Selected crystal	data, data collection and	refinement parameters for 1-5.
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	1	2	3	4	5
Formula	$C_8H_6O_4$	$C_8H_6O_4$	$C_8H_6O_4$	$C_8H_6O_4$	$C_{12}H_8O_4$
Molecular mass, M_r / a.u.	166.13	166.13	166.13	166.13	216.18
Temperature, T/K	100	100	100	250	100
Crystal system	Monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_{1}/n$	<i>P</i> -1	$P2_1 2_1 2_1$	<i>P</i> 2 ₁	$P2_{1}/n$
<i>a</i> / Å	3.7157(2)	7.4756(4)	4.7435(1)	3.8070(1)	15.5165(18)
<i>b</i> / Å	5.5117(2)	8.2973(5)	12.9275(2)	7.3986(2)	3.7812(1)
<i>c</i> / Å	16.3825(6)	11.9343(7)	22.1367(4)	12.5470(4)	16.046(3)
α / °	90	78.758(5)	90	90	90

β / °	93.399(4)	76.136(5)	90	95.445(3)	102.91(2)
γ / °	90	84.789(5)	90	90	90
Volume, $V/Å^3$	334.92(3)	704.14(7)	1357.46(4)	351.81(2)	917.7(2)
$d_{\rm calc}$ / gcm ⁻³	1.647	1.567	1.626	1.568	1.565
<i>F</i> (000)	172	344	688	172	448
Absorption coefficient, μ / mm^{-1}	1.158	1.102	1.143	1.102	1.003
No. of measured, independent reflections	2878 / 700	8615 / 2409	7438 / 2369	3284 / 1433	9403 / 1937
$R_{ m int}$ / %	2.08	1.28	2.49	1.78	2.15
GooF	1.036	1.050	1.050	1.059	1.058
$R[F] / wR[F^2] (I \ge 2\sigma(I)) / \%$	3.29 / 9.11	3.20 / 8.85	2.83 / 7.38	3.39 / 9.40	4.36 / 11.87
Max. and min. residual density / $e {\rm \AA}^{-3}$	-0.155 /0.287	-0.238 / 0.181	-0.230 / 0.161	-0.144/ 0.136	-0.263 / 0.282

CSD search. The Cambridge Crystallographic Database was searched using the CONQUEST⁶⁷ program (version 1.21). The search procedure included all compounds containing the salicylaldehyde fragment excluding ionic compounds and polymers (279 entries). Within this group 243 salicylaldehydes possess intramolecular O–H…O HB. Histogram representing O…O distance distribution is presented in SI (**Figure S1**).

Theoretical calculations

Single-molecule computation. Ab initio calculations were performed using Gaussian16 programme package.⁶⁸ In the first step the molecules were optimised in their ground states using M06-2X (DFT)⁶⁹ method with aug-cc-pVTZ⁷¹ basis set. The geometries of *N*-Me and *N*-Ph Schiff bases along with their corresponding boron complexes were optimised at the same level of theory. After geometry optimization, the vibrational frequencies were calculated and the results showed that optimized structures are stable geometric structures (no imaginary frequencies). Natural Bond Orbital (NBO) analysis was used to calculate Wiberg bond indexes and atomic charges. The O–H distance constrained optimisation energy scan was performed at the same level of theory. The O–

H distance was constrained on each step, while the rest of geometrical parameters were fully optimised (**Figure S7**). In the next step, the absorption process was simulated using TD-DFT methods (at $PBE0^{71} / 6-311++G(d,p)^{72}$). To take into account the conditions of absorption measurements (dilute DCM solution), calculations were carried out in the presence of the solvent (DCM) with the polarizable continuum model (PCM) using the polarizable conductor calculation model (CPCM).⁷³

Aromaticity indicators. Nucleus-independent chemical shift (NICS) were calculated for points located at the centre of the aromatic rings (NICS(0)) and the points 1Å above and below the centre of the ring. The latter values were averaged to yield NICS(1).⁷⁴ NICS are defined as the negative value of the absolute shielding computed at certain point. the NICS(0) values may contain important spurious contributions from the in-plane tensor components and are affected by the σ -bond density, so it was postulated that NICS(1) values better reflects aromaticity patterns. The harmonic oscillator model of aromaticity (HOMA) index was calculated according to the definition proposed by Kruszewski and Krygowski:⁷⁵

$$HOMA = 1 - \frac{\alpha}{n} \sum_{i=1}^{n} (R_{opt} - R_i)^2$$

where *n* corresponds to the number of bonds within the analysed ring, R_{opt} being a optimal bond length (1.396A from our calculations for benzene) and α was set to 257.7.

Topological analyses of electron density. The topological analyses of the calculated electron densities of all studied systems was prepared for the ground state optimised geometries at MP2⁷⁶/6- $311++G(d,p)^{72}$ level of theory. It was accomplished in terms of QTAIM approach⁷⁷ and was carried out using AIM2000 programme.⁷⁸ In the framework of this approach critical points (CPs)

together with the bond paths (BPs) were found. The bond critical points (BCPs) were analysed for intramolecular O-H...O HBs. The energy of the intramolecular HB interactions were estimated on the basis of empirical equations proposed by Rusinska-Roszak^{79–81} and further developed by Afonin.⁸² The equations correlates the energy of intramolecular HBs with H...O distance ($E^{d}_{O-H...O}$ = $f(d_{H...O})$) or are based on electron density value at BCP ($E^{p}_{O-H...O} = f(\rho_{(BCP)})$):

$$E^{\rm q}_{\rm O-H...O} = -15.27 d_{\rm H...O} + 34.02$$

 $E^{\rm p}_{\rm O-H...O} = 216.08 \rho_{\rm (BCP)} - 1.71$

Periodic calculations. All energy computations within the *CRYSTAL09* program package were performed at the DFT(B3LYP) level of theory with POB triple-zeta valence + polarization basis set (TZVP).⁸³ Grimme dispersion correction and correction for the basis set superposition error was applied.⁸⁴ Ghost atoms were selected up to 15 Å distance from the studied molecule in a crystal lattice, and were used for the basis set superposition error estimation. The evaluation of Coulomb and exchange series was controlled by five thresholds, set arbitrary to values of 10^{-7} , 10^{-7} , 10^{-7} , 10^{-7} , 10^{-7} , 10^{-25} . The condition for the SCF convergence was set to 10^{-7} on the energy difference between two subsequent cycles. Shrinking factor was equal to 4, which refers to 30-36 k-points (depending on space group symmetry) in the irreducible Brillouin zone in the case of the studied systems, and assures the full convergence of the total energy. The cohesive energy (*E*_{coh}) was calculated as described below:

$$E_{\rm coh} = \frac{1}{Z} E_{\rm bulk} - E_{\rm mol}$$

where E_{bulk} is the total energy of a system (calculated per unit cell) and E_{mol} is the energy of a molecule extracted from the bulk . Z stands for the number of molecules in the unit cell.⁸⁵

UV-Vis and fluorescence spectra

The UV-Vis absorption spectra were recorded using a Hitachi U-2300II spectrometer. The emission spectra of solutions were recorded using a Edinburgh FS5 spectrofluorometer, equipped with an extended range photomultiplier detector (PMT-EXT). The measurements were performed at room temperature, according to published procedures.^{87,88} Suprasil quartz cuvettes (10.00 mm) were used. 1.5 nm slits were used for absorption and 1.0 nm slits were used for emission spectra. To eliminate any background emission, spectrum of pure solvent was subtracted from the samples' spectra. qy was determined in diluted solution (c = $1 \cdot 10^{-5}$ mol·dm⁻³) by comparison with known standard – coumarin 153 in ethanol (c = $4 \cdot 10^{-6}$ mol·dm⁻³, qy = 0.544).⁸⁸ Sample was excited at 418 nm. Quantum yield was calculated using following equation:

$$qy_{x} = qy_{st} \cdot \frac{F_{x}}{F_{st}} \cdot \frac{1 - 10^{-A_{st}}}{1 - 10^{-A_{x}}} \cdot \frac{n_{x}^{2}}{n_{st}^{2}}$$

where F is the relative integrated photon flux of sample (**x**) and standard (**st**), A is the absorbance at the excitation wavelength, n is the refractive index of used solvents. Photon fluxes (F) were calculated by integration of corrected spectra (I_c)

$$F = \int I_{\rm c} \, d\lambda_{\rm em} = \int \frac{I(\lambda_{\rm em})}{s(\lambda_{\rm em})} d\lambda_{\rm em}$$

Results and Discussion

Synthesis

1,4-Diformyl-2,5-dihydroxybenzene (1) and 1,4-diformyl-2,3-dihydroxybenzene (3) were prepared by double metalation of 1,4- and 1,2-dimethoxybenzenes with *n*-BuLi, followed by reaction with DMF, and subsequent removal of the methyl groups with BBr₃.⁵⁹ The same strategy applied to 1,3-dimethoxybenzene is known to metalate mainly at 2-position,^{89,90} thus in the first step the arene was brominated to obtain 1,3-dibromo-4,6-dimethoxybenzene, and then double halogen-metal exchange at specific positions gave dialdehyde **2**.⁵⁹

In turn, synthesis of 2,3-diformyl-1,4-dihydroxybenzene (**4**) was not previously described in the literature, although numerous derivatives of **4**, bearing additional substituents present at positions 5 and 6, are known.⁹¹ In contrast to syntheses of the remaining isomers **1-3**, preparation of **4** would require a double metalation of 1,4-dimethoxybenzene at adjacent positions 2 and 3, that is disfavored due to the Coulombic forces.⁹² Our initial approach assumed introduction of the formyl group to 2,5-dimethoxybenzaldehyde, using methodology developed by Comins.^{93,94} Accordingly, the formyl group was transformed to the lithium salt of *N*,*N*,*N'*-trimethylethylenediamine, giving an adduct, which then was treated with excess of *n*-BuLi, and quenched with DMF. Chelating part of the diamine is known as *ortho-directing* group in metalations, and was utilized for functionalization of *m*-anisaldehyde at the position 2.⁹⁴ However, in our hands dimethoxy analogue **6** underwent metalation only at positions 3 and 4 (directed by the OMe groups), instead of the expected internal position 6 (**Scheme 1**, below).⁹⁵



Scheme 1. Attempt at metalation-formylation of 2,5-dimethoxybenzaldehyde (6) according to Comins methodology.^{93,94}

Therefore we changed the synthetic plan and used commercially available 2,3-dicyanohydroquinone as a substrate. Butylation of the phenolic oxygen atoms,⁹⁶ followed by hydrolysis of the nitrile groups, and reduction with LiAlH₄ gave diol **9** in 70% overall yield. Then, Swern oxidation, followed by cleavage of the ethereal bonds gave desired dialdehyde **4**, whereas

attempts at oxidation of 9 with PCC led exclusively to lactone 10, isolated in 76% yield (Scheme

2).



Scheme 2. Successful synthesis of 2,3-diformyl-1,4-dihydroxybenzene (4).

Interestingly, the 2,3-diformyl-1,4-dihydroxybenzene (**4**) appeared to be stable, and few mm size crystals were grown by slow evaporation of its chloroform solution in open glass vial under air. Finally, 2,7-diformyl-1,8-dihydroxynaphthalene (**5**) was prepared according to a 4-step procedure involving double bromine/lithium exchange in 1,5-bis(methoxymethoxy)-2,6-dibromonaphthalene followed by quenching with DMF and hydroxyl groups deprotection.³⁵

Molecular properties of 1-5

Single crystals of bis(salicylaldehydes) were obtained by slow evaporation of the corresponding acetone solutions and investigated by X-ray diffraction. Molecular structures are presented in **Figure 1**. Molecules **1**, **2** and **5**, laying on the inversion center, crystallize in centrosymmetric space group ($P2_1/n$ or P-1), whereas **3** and **4** which are located on the two-fold axis, crystallize in non-centrosymmetric space groups $P2_12_12_1$ and $P2_1$, respectively. All molecules are essentially planar reflecting effective conjugation between substituents and the benzene ring. Their metric features are in the range expected for such aromatic derivatives. In case of compounds **2**, **3** and **5**, two symmetrically independent molecules (abbreviated **2a/2b**, **3a/3b**, **5a/5b**) were observed. In case of **2** and **5**, their geometries differ only marginally. Unexpectedly, molecule **3b** features only

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one intramolecular RAHB. The second formyl group is oriented *anti* with respect to the adjacent OH substituent which in turn is engaged in an intramolecular HB with the neighbouring OH group



Figure 1. X-ray molecular structures of **1-5** with the labelling scheme (only asymmetric part). Displacement ellipsoids are drawn at the 50% probability level. Note that **4** was exceptionally measured at 250 K, remaining structures were measured at 100 K.

Hydrogen atoms from the OH group were refined freely only constraining their isotropic displacement parameters with respect to oxygen atoms. Fourier difference density maps show that they reside exclusively on the hydroxyl site (**Figures S2-S6**, Supporting Information). Theoretical calculations show that proton transfer is rather not favoured (**Figure S7**, SI), nevertheless, significant O...O bond shortenings ($d_{O...O} = 2.588-2.709$ Å) with respect to intermolecular HBs

 $(d_{0...0} = 2.7-3.0 \text{ Å})$ originate from RAHB, as observed by Gilli and others for many salicylaldehydes and conjugated β -diketo enols.^{23-24,28} A closer inspection of geometries of intramolecular OH...O=C bridges (Table 2) reveals significant differences between 1-5. The weakest OH...O=C bridge was found for 1 (2.709(1) Å), whereas the strongest one is observed for 4 (2.588(3) Å) and 5 (2.591(2) Å). The CSD analysis revealed that those distances are typical for other salicylaldehydes (Figure S1, SI). However, the strength of the intramolecular HB in crystal structure is influenced to some extent by the intermolecular interactions with neighbours. Furthermore, structure 4 was exceptionally measured at 250 K as the crystal collapsed below this temperature presumably due to phase transition. Thus, to quantitively compare the intramolecular HBs in studied systems, the use of geometries derived from single-molecule DFT (M06-2X/augcc-pVTZ) optimizations seemed to be more reliable. Indeed, in the case of 1, significant shortening of the O...O distance (to 2.664 Å) is observed and it is comparable to the corresponding O...O distances in salicylaldehyde (A) and structure 3. We have found that the strength of RAHB is significantly influenced by mutual resonance interactions of electron-withdrawing formyl and electron-donating hydroxyl groups. In compound 1, the formyl groups are in the para position to each other, which decreases the H-bond acceptor ability. Simultaneously, the hydroxyl groups are also in the *para* position one to another which results in their reduced acidity consistent with weaker H-bond donor properties. Similarly, in 3 the formyl groups are in the *para* position, whereas hydroxyl groups are in ortho positions. Thus, in both cases cumulation of resonance effects results in relative weakening of the RAHB. In contrast, in 2 the cooperation of mesomeric effects is observed resulting in enhancement of proton acceptor character of the CHO groups and acidity of the OH groups. In case of 4, the location of hydroxyl and formyl groups causes the opposite resonance effects somehow puzzling the observed significant shortening of the O...O

distance in this system ($d_{0...0} = 2.570$ Å). However, it can be rationalized by the steric repulsion of *ortho* positioned formyl groups ($d_{H...H} = 2.035$ Å), which is also reflected by the deformation of C2–C1–O1(OH) and C1–C2–C7(CHO) bond angles. The influence of mesomeric effect is also clearly visible for naphthalene system **5**. Although naphthalene monoaldehyde (**B**) is characterized by shorter O...O distance with respect to salicylaldehyde **A**, introduction of hydroxyl groups at the position 5 reduces the acidic character of both groups leading to elongation of O...O distance in intramolecular HBs.

The O–H...O bond distances correlate with the electron density values at O–H...O bond critical point (ρ (BCP)) calculated at MP2/6-311++G(d,p) level of theory (**Table 2**, **Figure S8**, SI). Consequently, in **1** the ρ (BCP) equals to 0.231 eÅ⁻³ and is lower than for **A**, then it increases following the order **3** < **2** < **5** to reach 0.295 eÅ⁻³ for **4**. Similar trend is observed for the Laplacian (**Figure S9**, SI). These observations are consistent with well described continuous relations of both functions (ρ (BCP), $\nabla^2 \rho$ (BCP)) on bond path length.⁹⁷ On the basis of calculated O...O distance and electron density values we have estimated the energy of the intramolecular HB using empirical equations proposed by Afonin.⁷³ According to these calculations the energies of single intramolecular HB in **1-5** oscillate between 24-33 kJmol⁻¹. It should be noted that in the case of **4**, the high value of electron density partially results from the H...H repulsion between formyl groups. Thus the strength of RAHB is overestimated. The removal of hydrogen atoms followed by the optimisation in triplet state (**4**[•])⁹⁸ provided more reasonable values of electron density and energy of RAHB. According to these computations the electron density drops from 0.295 eÅ⁻³ to only 0.223 eÅ⁻³ after release of steric repulsion.

Table 2. Characterization of intramolecular H-bonding interactions for the salicylaldehyde motifs
in 1-5 derived from the experimental single crystal XRD data (Exp) and theoretical calculations
(Theor). Topological parameters derived from QTAIM theory at O-HO Bond Critical Points
(BCPs) together with estimated interaction energies. d - distance; α - angle, ρ - electron density;
$\nabla^2 \rho$ - Laplacian; $E^{d}_{\text{O-HO}}$, $E^{\rho}_{\text{O-HO}}$ - interaction energy derived from empirical equations proposed
by Afonin.

/									
8	$d_{\text{O}\dots\text{O}}^{\text{Exp}}$	d_{00}^{Theor}	$d_{\text{OH}}^{\text{Theor}}$	$d_{\text{O-H}}^{\text{Theor}}$	α_{O-HO}^{Theor}	$\rho(\text{BCP})$	$\nabla^2 \rho(\text{BCP})$	<i>Е^d</i> о–н…о	<i>Е</i> ^{<i>р</i>} о–н…о
9 0 1	/ Å	/ Å	/ Å	/ Å	/ °	/ eÅ ⁻³	/ eÅ ⁻⁵	$/ kJ \cdot mol^{-1}$	$/ kJ \cdot mol^{-1}$
A 2	2.623	2.645	1.785	0.978	144.91	0.248	2.87	25.4	26.1
5 5 6	-	2.586	1.725	0.981	144.35	0.284	3.02	29.0	30.9
7 B 9	2.709(1)	2.664	1.817	0.973	143.64	0.231	2.87	23.4	23.8
0 ^a 1 2	2.651(1), 2.656(1), 2.652(1), 2.652(1)	2.630	1.758	0.981	146.06	0.264	2.88	27.0	28.2
3 a 4	2.641(2), 2.599(2),	2.644	1.791	0.977	144.00	0.246	2.92	25.0	25.7
5	2.615(2)								
4 8	2.606(3), 2.588(3)	2.570	1.707	0.980	144.75	0.295	3.09	30.1	32.4
0 ¶? ∩	-	2.679	1.833	0.979	142.79	0.223	2.45	21.9	23.3
5 ^a 2	2.613(2), 2.591(2)	2.622	1.762	0.982	144.16	0.261	2.92	26.8	27.8

^a two independent molecules in the unit cell

Theoretical calculations confirmed that for all studied compounds, conformations featuring RAHB are the most stable (**Table 3**). However, in case of **3**, the energy of a conformer consistent with the structure **3b** (showing the contact between formyl hydrogen and oxygen atom of the *anti*-oriented OH group) is only 6.6 kJmol⁻¹ higher. This small difference reflects the stabilization

provided by the intramolecular H-bond between neighbouring hydroxyl groups. It should also be noted here that the RAHB in the X-ray molecular structure **3b** is relatively stronger ($d_{0...0}$ = 2.615(2) Å vs $d_{0...0}$ = 2.727(2) Å). It can be explained by the effect of adjacent hydroxyl group forming another H-bond with the OH group participating in RAHB. As a result, acidity character of the latter OH group is increased, which, in turn, enhances its H-bond donor character. In addition, comparison of total energies of the most preferred conformations (i.e., possessing two RAHB motifs each) of **1-4** shows that compound **2** is much more stable (by ca. 35-48 kJmol⁻¹) than its isomers. It seems that this effect is due to the resonance interactions of formyl and hydroxyl groups which are in the *para* positions with respect to each other. Thus, an extra-stabilization would be provided by the charge transfer which occurs preferably in the *p*-quinoid-type structures comprising electron-donating and electron-withdrawing substituents.

Table 3. Comparison of conformational energies related to the most stable form within each system calculated at M06-2X/aug-cc-pVDZ level of theory. Conformation of one CHO/OH pair varied, while conformation of second pair was set to OH...OCH. Additionally, the most stable conformations are compared between isomers. All values are given in kJmol⁻¹.



2	0.0	31.9	44.0	40.1	0.0
3	0.0	6.6	20.3	36.4	37.7
4	0.0	25.1	48.6	45.4	48.3

Observed resonance effects have naturally a strong impact on the C–C bond lengths in the aromatic ring. Figure 2 presents the C-C bond lengths together with calculated Wiberg bond indexes derived from NBO analysis (M06-2X/ aug-cc-pVTZ). In salicylaldehyde A aromatic C-C bond linking the OH and CHO groups is longer with respect to other C-C bonds reflecting contribution of the keto-enol resonance structure. Similar relation is observed for molecules 1 and 2. This resembles bond relations in anthracene molecule, where endocyclic C-C bonds are elongated (1.438 Å) with respect to other C-C bonds.⁹⁹ Calculated bond indexes clearly show that deformation of aromatic ring geometry is more pronounced in the case of **3** and **4**. The C–C bonds between carbon atoms bearing OH and CHO groups (C1–C2 and C3–C4) become slightly shorter which is accompanied by elongation of neighboured C-C bonds. This is followed by strong localization of π -electron density at C5–C6 bond with bond indexes of 1.531 (3) and 1.552 (4). Interestingly, this resembles the bond situation of the inner ring in phenanthrene,¹⁰¹ where C9– C10 and C4a–C4b bond distances (i.e., the opposite bonds from inner phenantrene ring bisecting the two-fold axes) are 1.373 Å and 1.448 Å, respectively. Similar conclusions can be also drawn from the comparison of naphthalene bis(salicylaldehyde) **5** and chrysene molecule.¹⁰² The C1–C2 and C3–C4 bond lengths in 5 equal to 1.386 Å and 1.360 Å, respectively. In chrysene the analogous bonds distances are 1.417 Å and 1.356 Å, showing strong localization of the electron density in the latter bond. Summing up, bis(salicylaldehydes) exhibit some molecular features of the PAH molecules, thus by this sense it is reasonable to regard them as PAHs quasi-aromatic topological analogues.23



Figure 2. Comparison of bond lengths and Wiberg bond indexes (given in *italic*) for 1-5 and referential salicylaldehydes (A, B) (geometries optimized at B3LYP/6-311+G(d,p)). Red and yellow colors indicate bond shortening and elongation, respectively.

The changes in bond lengths are quite informative in connection with a geometrical criterion of local aromaticity. In order to compare aromatic characters of the studied systems, we have employed two popular aromaticity indicators: harmonic oscillator model of aromaticity (HOMA)⁷⁵ and nucleus-independent chemical shift (NICS)⁷⁴ The latter parameter was derived from calculations of the magnetic shielding (taken with a negative value) at the centroid of the aromatic ring (NICS(0)) and 1 Å above the centroid (NICS(1)). Calculations were performed at M06-

2X/aug-cc-pVTZ level of theory. In general, rings with large negative NICS values are considered aromatic and the aromaticity increases with the decrease (toward more negative values) of the NICS parameters. Calculated values show that the substituent effects have strong impact on the aromaticity character of the molecules (Table 4). For all studied bis(salicylaldehydes) loss of aromaticity was reflected by lower values of HOMA parameter. This is especially visible for compounds 2 and 4 owing to important contribution of p-quinoid-type resonance structure in the first example, and to the ring deformation due to formyl-formyl repulsion in the second case. Thus, the HOMA index drops from 0.965 for 1 to 0.847 for 4. Furthermore, obtained results suggest interference between HOMA and energy of intramolecular HB. Strengthening of the RAHB induces decrease of the HOMA index (Figure S10, SI). Qualitatively similar conclusions can be derived from the analysis of NICS values. First of all, the reduction of aromaticity in salicylaldehyde A is accompanied by the increase of NICS(0) and NICS(1) values with respect to benzene. In case of 1 and 3, the aromatic ring current becomes stronger which can be ascribed to positive mesomeric effects of *para* (1) and *ortho* (3) positioned hydroxyl groups. In case of 4, the effect becomes weaker, probably resulting from above discussed deformations of aromatic ring reflected by small HOMA values, while for molecule 2, both NICS values significantly increase confirming augmented contributions of CHO/OH pseudorings in π -electron delocalization.

Regarding the naphthalene derivatives, HOMA and NICS indicators suggest that the introduction of one CHO/OH pair (structure **B**) hardly affects the aromatic character of salicylaldehyde ring, but aromaticity increases in unsubstituted one. The addition of second CHO/OH pair realized in structure **5**, averages the HOMA indexes of both rings as compared with monohydroxyaldehyde **B**. On the other hand, NICS parameter suggest that aromatic character of **5** is weaker with respect to monoaldehyde and naphthalene. We have also calculated the magnetic

shielding constants in the points located 1 Å above central hydrogen-bonded quasi-aromatic rings. For benzene-based bis(salicylaldehydes) obtained NICS(1) values negatively approach to zero. In contrast, in **B** and **5** they adopt slightly positive values.

Table 4. Aromaticity indicators. HOMA parameters are calculated from X-Ray experimental and optimized geometries. NICS(0) and NICS(1) are based on optimized geometries. NICS(1)^{RAHB} relate to hydrogen bonded ring (for 1-5 calculated as average value).

	HOMA ^{Exp}	HOMA ^{Theor}	NICS(0)	NICS(1)	$NICS(1)^{RAHB}$
Benzene	1	1	-9.82	-11.31	-
Α	0.971	0.967	-9.18	-9.63	-0.07
1	0.935	0.965	-10.50	-9.90	-0.19
2	0.896 / 0.900 ^a	0.895	-7.92	-8.04	-0.16
3	$0.932 \ / \ 0.940^a$	0.913	-10.22	-9.60	-0.20
4	0.850	0.847	-9.49	-9.12	-0.36
Naphthalene	0.858 ^b	0.833	-10.10	-11.68	-
В	-	0.834/0.882 ^c	-9.42/-11.24 ^c	-9.51/-11.27 ^c	0.10
5	0.832/0.836 ^a	0.856	-8.86	-9.66	0.09

^aTwo independent molecules in the unit cell; ^bgeometry taken from lit.¹⁰² ^cSalicyl/distant aromatic rings.

Comparison of atomic charges (computed by the NBO method) shows that molecule **2** experiences highly anisotropic distribution of the electron density in the aromatic ring (**Figure 3**). Except for **2**, in all systems carbon atoms bearing hydroxyl group are positively charged of about +0.34 e and magnitude of negative charge on the remaining carbon atoms oscillates near -0.2 e. In contrast, in **2** the cooperative positive mesomeric effects of hydroxyl groups induce high negative charge on carbon atom located at *ortho* position to both groups (-0.31 e). Simultaneously, formyl

groups withdraw the electron density from *ortho-* and *para-* positions increasing charge on C–OH carbon atoms to +0.42 e and carbon atom located in between these two groups, which become less negative (-0.07 e).



Figure 3. NBO atomic charges for aromatic carbon atoms together with dipole moment vector and its magnitude. Positive and negative charges are depicted in green and blue colors, respectively. Intensity of the color corresponds to the charge magnitude.

The variations in charge distribution should also affect the molecular orbitals levels and, in consequence, UV-Vis spectral properties. According to our suppositions, there is a distinct difference between UV-VIS absorption spectrum of compound **2** and the spectra of remaining isomers as in the first case there is no absorption in the visible range (**Figure 4**, **Table 5**). As a result, **2** is colorless, whereas other compounds have an intense yellow colour. The spectrum of **2** shows three distinct bands in the UV range at 256, 288 and 325 nm. The longest wavelength absorption bands (λ_{max}) for **1**, **3**, **4** are ranging from 400-423 nm with quite high molar absorption coefficients (ε = 3500-8500 M⁻¹ cm⁻¹).

TD-DFT calculations of absorption spectra (PBE0/ 6-311++G(d,p)) show that these bands are attributed to π - π * HOMO-LUMO transition.

Among studied series, compound **5** is characterized by the longest wavelength of absorption (439 nm) and the highest molar absorption coefficients ($\varepsilon = 9700 \text{ M}^{-1} \text{ cm}^{-1}$). Interestingly, we have found that UV-Vis spectra of previously studied by us Schiff base organoboron complexes, namely bis(boranils),³⁴ qualitatively match to spectrum of parent bis(salicylaldehyde) **5**. Furthermore, **5** is strongly luminescent, emitting light with maximum at 506 nm and quantum yield of 0.60 in DCM. At this point it is noticeable, that naphthalene-based bis(boranils) are characterized by exceptionally high quantum yields (up to 83%), that presumably results from molecular features (i.e. substitution pattern, structural stiffness) of parent bis(salicylaldehyde) **5**.

Regarding the most intriguing system 2, the longest absorption band results from the transition between HOMO and LUMO levels with some contribution from HOMO-1 to LUMO states, however, the calculations show that HOMO level is significantly lowered, while LUMO level is elevated with respect to remaining molecules (**Figure 5**). This results in the increase of band gap and observed hypsochromic shift of the absorption band. We have found that the differences in HOMO and LUMO levels are attributed to mesomeric effects of hydroxyl and formyl groups, respectively, and those effects seem to operate independently to some extent. To support this thesis, we have performed computations for *para*, *meta* and *ortho* isomers of dihydroxybenzene, diformylbenzene and hydroxybenzaldehydes (9 structures in total). Results of these computations are presented on **Figure S12** in SI. Comparing the energy levels in a series of isomeric dihydroxybenzenes, the lowering of the HOMO orbital is clearly visible in *m*-dihydroxybenzene. In turn, the LUMO level is elevated in isophthalaldehyde (*m*-diformylbenzene). It is also noticeable that the energy gap decreases in series of p-, *m*-, *o*-

hydroxybenzaldehyde, and further decreases in bis(salicylaldehydes) following the order 3 > 4 > 5 to reach 3.33 eV for compound 1.

To address the question whether the structure-property relation in bis(salicylaldehydes) is transferable to other systems such as Schiff bases, we have extended our research by studying corresponding *N*-Ph and *N*-Me diimines, and their boron BF₂ complexes. According to our computations (M06-2X/aug-cc-pVT)), all spectroscopic trends are preserved in those systems (**Figures S13-16**, SI). Furthermore, aromatic character of bis(salicylaldimines) and their BF₂ complexes monitored by HOMA and NICS values follows the same trend as observed for their aldehyde precursors (**Figure 6**, **Table S1**, **Figures S17-S22**, SI). It is thus supposed that the observed trends would be preserved in other systems to some extent, although one have to keep in mind that the introduction of strong electron-donating or electron-withdrawing substituent may shuffle the orbital scheme.



Figure 4. UV-Vis absorption spectra of **1-5** in DCM supplied by insert of normalized spectra (left) and overlay of emission and absorption spectra of **5** in DCM (right).

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Table 5. Optical properties of compounds 1-5.

	Experime	ntal		TD-DFT	
Compound	solvent	$\lambda_{\rm max}/{\rm nm}$	$\varepsilon / M^{-1} \text{ cm}^{-1}$	λ_{abs}/nm	F
1	DCM	278	31000	254	0.402
		423	7000	409	0.109
2	DCM	256	65000	235	0.456
		288	14000	259	0.267
		325	5000	287	0.109
3	DCM	284	27000	250	0.268
		400	3500	384	0.168
4	DCM	263	13500	247	0.189
		408	8500	389	0.127
5	DCM	266	103300	254	1.308
		304	13100	285	0.189
		439	9700	400	0.173



Figure 5. Diagram showing calculated frontier orbital levels in all studied systems.



Figure 6. Comparison of NICS(1) indexes in series of bis(salicylaldehydes), their *N*-Me Schiff bases, and corresponding BF_2 complexes. Numerical values are deposited in Table S1 in SI.

Structural analysis

The first level of supramolecular organization in crystal structures of **1**, **2** and **4** is based on the O–H…O HB interactions. The OH groups act as intra- and intermolecular double donor of HB to

formyl groups. And *vice versa*, carbonyl oxygen atoms are bifurcated by two OH groups. The aggregation through O–H…O HBs is, however, not obvious, as all OH hydrogen atoms are engaged in intramolecular HBs, thus decreasing their potential involvement in intermolecular contacts. For instance, in structures **3** and **5**, the intermolecular O–H…O HBs are rather avoided, and they are replaced by C–H…O and specific C=O…C(π)HO contacts between perpendicularly aligned carbonyl groups.

For quasi-aromatic analogues of anthracene, the linear molecular geometries favor the formation of HB centrosymmetric dimers, which further propagate to 1-dimensional chains. This motif is observed in crystal structure of 2. Alternatively, in 1 the molecules are mutually displaced in chains - each molecule interacts with four neighbours via single HB interaction. The propagation of this motif leads to the formation of 2-dimensional sheet (Figure 7). Interactions between sheets are mostly dominated by C(Ar)-H...O and C(π)...C(π) interactions. Similar forces are responsible for supramolecular assembly in 2. In this case the $C(\pi)...C(\pi)$ interactions between adjacent HB [010] chains are operating along [100] direction, while in [001] direction the molecules are linked by C(O)H...OCH contacts formed between formyl groups of adjacent molecules. As a result, the crystal packing can be described as a set of layers, each composed of parallelly oriented molecules and rotated by 90 deg with respect to molecules from adjacent layers (Figure 8). The crystal structure of 4 shows a similar packing pattern. On the first level of structural organization, the molecules form hydrogen-bonded chains which further propagate through C(O)H...O and $C(\pi)...C(\pi)$ interactions (Figure 9). The only difference relies on the HB pattern within the molecular chains. Hydroxyl group of one molecule plays a role of acceptor and donor of HB to hydroxyl and formyl groups of the second molecule. As a result, the formyl group from the first molecule does not participate in the intermolecular O-H...O HB. Instead, it is arranged in a

bifurcated C(O)H...O interactions with two *ortho*-positioned formyl groups from neighboured molecule.

The most distinct structural motifs are observed in crystal structures **3** and **5**. In case of **3**, the HB between hydroxyl groups link molecules **3a** and **3b** into dimers. In turn, formyl groups are involved in two types of interactions: C(O)H...O interactions with hydroxyl oxygen atom, and also C=O...C(O)H interaction between formyl oxygen atom and electron deficient carbon atom from neighboured CHO group. The propagation of the latter interaction along [100] direction leads to linear herringbone-type arrangement (**Figure 10**). This motif dominates the crystal structure of **5**. It is additionally supported by $C(\pi)...C(\pi)$ interactions formed between electron-deficient CHO carbon atom and electron-rich aromatic ring carbon atom bearing the CHO group (**Figure 11**).



Figure 7. Crystal packing of 1 showing (100) H-bond layer formation (*a*) and its further aggregation through dimeric C–H...O and π - π interactions. Red dotted lines correspond to HBs.



Figure 8. Packing diagram for **2** showing the formation of H-bonded chains and their further aggregation through C–H...O and π - π interactions.



Figure 9. Supramolecular structure of 4.



Figure 10. Supramolecular structure of **3** showing the formation of hydrogen-bonded dimers (a) and herringbone arrangement resulting from π -stacking and C=O...C(O)H interactions.



Figure 11. Herringbone molecular arrangement in crystal structure 5.

To get deeper insight into the structural relation in isomeric bis(salicylaldehydes) 1-4 we have performed periodic density functional calculations at B3LYP/TZVP level of theory using CRYSTAL09 program. During the optimization, the unit cell parameters were constrained while positions of the atoms were fully optimized. This procedure allowed us to obtain more reliable positions of the hydrogen atoms. The obtained cohesive energy values (E_{coh}), which comprise crystal field stabilization effects, and the total crystal energies (ΔE_{tot}), which sum the contributions from the molecular energy and intermolecular interactions, related to the energy of most stable

system are presented in **Table 6**. Regarding E_{coh} values, all bis(salicylaldehydes) are more stable than salicylaldehyde **A** resulting from extra-stabilization from the intermolecular interactions with additional CHO and OH groups. Furthermore, Crystal09 computations reveal that crystal structures **1** and **3** are characterized by the most favourable cohesive energy value of -145.4 kJmol⁻¹. Structures **2** and **4** are the next in line as E_{coh} values oscillate near -130 kJmol⁻¹ reflecting their similarities.

Total crystal energy derived from Crystal09 computations (ΔE_{tot}) comprises both single molecule and crystal field stabilization effects. The comparison of ΔE_{tot} values shows that the structure **2** is the most stable among the studied series. Its lower cohesive energy is counterbalanced by the very advantageous molecular energy resulted from cooperative resonance effects of hydroxyl and formyl groups operating in this molecule (**Table 3**). In case of **1** and **3** both energetic effects are of similar magnitude thus leading to comparable total crystal energy. Finally, **4** is characterized by less favorable intra- and intermolecular energy contributions.

Table 6. CRYSTAL09-derived cohesive energies (E_{coh}) corrected with BSSE and Grimme dispersion corrections and total crystal energy comparison between 1-4 (ΔE_{tot}) related to the energy of the most stable system (2).

	А	1	2	3	4	5
$E_{\rm coh}/{\rm kJmol^{-1}}$	-104.5	-145.4	-132.1ª	-145.4 ^a	-128.2	-114.7
$\Delta E_{\rm tot}$ / kJmol ⁻¹	-	27.6	0	27.2	39.0	-

^aAveraged value per one molecule.

Conclusions

In summary, we have presented detailed investigations on the structure-energy-property relationships for the series of isomeric bis(salicylaldehydes). They represent the simplest set of model multifunctional hydroxyaldehydes which are currently extensively used as a building units for the construction of various functional materials. Therefore, particular attention should be paid to their molecular properties. Consequently, we have considered two leading co-dependent aspects of their molecular features: (1) intramolecular HB and (2) resonance effects of hydroxyl and formyl groups operating in the molecule. As indicated by theoretical calculations, strength of the RAHB is significantly influenced by mutual resonance interactions of formyl and hydroxyl groups. Cooperation of push-pull mesomeric effects results in the strengthening of the HB, while competition of the same sight resonance effects results in the weakening of intramolecular HB. In addition, the mutual interactions between *ortho* located groups of the same type (OH or CHO) may also influence the RAHB. This is demonstrated by system 3, where possibility for the formation of intramolecular O–H...O bond between hydroxyl groups increases the conformational lability of this molecule. In the case of 4, an intramolecular repulsion between formyl groups leads to molecular deformation and, eventually, to strengthening of HB. The influence of mesomeric effect on the intramolecular bond properties is also visible in naphthalene-based systems **B** and **5**, however, due to higher distance between CHO and OH groups these effects are weaker with respect to 1-4. Our calculations also demonstrate decreased aromatic character of bis(salicylaldehydes) 1-5 with respect to mono(salicylaldehyde) and benzene/naphthalene. The HOMA index changes from 0.965 for 1 to only 0.847 for 4. This correlates with the strength of HB interactions and depends on the cooperative/competitive character of mesomeric effects. This is especially visible for isomer 2, which is the most stable system in a studied series reflecting cooperation of resonance effects from OH and CHO groups. The molecule of 2 is also

characterized by the most anisotropic charge distribution and orbital energy levels differentiation. The HOMO energy level is lowered in this system, while LUMO is elevated with respect to remaining isomers leading to strong hypsochromic shift of the absorption band. Importantly, we have proven that the observed dependences are directly transferable to related diimines and their boron complexes. It can be thus concluded that spectral properties of such systems directly result from the structural features of parent bis(salicylaldehydes).^{35,39}

ASSOCIATED CONTENT

Supporting Information. CSD basis search analysis, residual density maps for structures **1-5**, O-H...O constrained optimization energy scan, correlation plots, frontier orbitals diagrams for Schiff bases, boron complexes, dihydroxybenzenes, phthalaldehydes and hydroxybenzaldehydes, Cartesian coordinates for all optimized structures of biss(salicylaldehydes), comparison of HOMA and NICS parameters between bis(salicylaldehydes), Schiff bases and corresponding boron complexes, description of our attempts at synthesis of **4** by metalation-formylation of 2,5dimethoxybenzaldehyde, copies of NMR spectra of new compounds.

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TOC Graphic

