

CRYSTAL AND MOLECULAR STRUCTURE OF *N*-(3,5-DICHLORO-2-HYDROXYBENZYLIDENE)- AND *N*-(2-HYDROXY-3-METHOXYBENZYLIDENE)ANILINE OXIDES. DELOCALISATION IN THE SPACER OF THE INTRAMOLECULAR H-BOND AND THE PROBLEM OF QUASI-AROMATICITY

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Dedicated to Professor Otto Exner on the occasion of his 75th birthday.

The hydrogen bond in the title compounds and their analogues with the spacer built of six heavy atoms (O,N,C,C,C,O) between the H-donor OH group and H-acceptor oxygen atom in the oxide group is much stronger than in the case of spacers with five heavy atoms. In spite of that, the delocalisation in the spacer does not depend on the strength of the H-bond, leading to the conclusion that quasi-aromaticity is not a proper term for these kinds of pseudorings. This is supported by analysis of the geometry of *N*-(3,5-dichloro-2-hydroxybenzylidene)- and *N*-(2-hydroxy-3-methoxybenzylidene)aniline oxides presented in this study and molecular geometries of five well solved structures retrieved from the CSD. Schleyer's index of aromaticity, NICS, is positive (*i.e.* indicating nonaromatic behaviour) for a model approximating the title H-bond system spacer indicating no ring current in the pseudoring whereas Li⁺-chelated system exhibits a slightly aromatic property (NICS < 0).

Key words: H-Bonds; Aromaticity; Schiff bases; Chelates; Crystal structure; X-Ray diffraction; *Ab initio* calculations.

In continuation of our structural studies on Schiff bases¹, we have focused here on those which contain a six-membered spacer between the hydrogen donor and acceptor, which is drawn in bold lines in Fig. 1.

Due to their interesting properties, Schiff bases are the subject of many structural and physicochemical studies¹⁻⁶. While the properties of the hydrogen-bond are the subject of many studies²⁻⁶, much less is known about the π -electron structure of the heavy atom skeleton building up the spacer between the H donor and H acceptor¹. This part of the molecule might be considered as a quasiaromatic one^{7,8} and the question arises which factors mostly influence the π -electron delocalisation in this fragment. In the previous paper dealing with Schiff bases with OH...N bridge and the five-membered heavy atom spacer, it was shown¹ that the π -electron delocalisation in the spacer depends on the substituent effects, whereas the other factors are of less importance.

The aim of this report is to consider this problem taking into account the systems with a stronger intramolecular H-bond. To tackle this, we extended our own results on the X-ray-measured molecular geometry of *N*-(3,5-dichloro-2-hydroxybenzylidene)- and *N*-(2-hydroxy-3-methoxybenzylidene)aniline oxides **1** and **2** with the data of analogous structures retrieved from the Cambridge Structural Database⁹ and supported by *ab initio* calculations¹⁰.

EXPERIMENTAL

The X-ray measurements of single crystals of *N*-(3,5-dichloro-2-hydroxybenzylidene)- and *N*-(2-hydroxy-3-methoxybenzylidene)aniline oxides were carried out on a KM-4 KUMA diffractometer with graphite monochromated CuK α radiation. The data were collected at room temperature using the ω -2 θ scan technique. The intensity of the control reflections varied by less than 3%, and the linear correction factor was used to account for this effect. The data were also collected for Lorentz and polarisation effects and absorption correction was used¹¹. The structure was solved by direct methods¹² and refined using SHELXL (ref.¹³). The refinement was based on F^2 for all reflections except those with very negative F^2 . The weighted R factor, wR , and all goodness-of-fit S values are based on F^2 . The non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were placed in the calculated positions, and their thermal parameters were refined isotropically. The hydrogen atoms participating in H-bond were found from the map and refined. The atomic scattering factors were taken from the International Tables¹⁴. Details of the X-ray measurements and crystal data for both title compounds are given in Table I, whereas their ORTEP scheme and

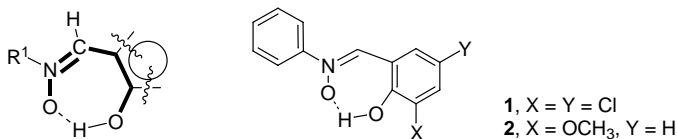


FIG. 1

Scheme of systems studied in this paper

TABLE I

Crystal data and structure refinement for *N*-(3,5-dichloro-2-hydroxybenzylidene)- (1) and *N*-(2-hydroxy-3-methoxybenzylidene)aniline oxides (2)

Parameters	1	2
Empirical formula	C ₁₃ H ₉ Cl ₂ NO ₂	C ₁₄ H ₁₃ NO ₃
Formula weight	282.11	243.25
Temperature, K	293(2)	
Wavelength, Å	1.54178	
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions: <i>a</i> , Å	13.317(3)	8.906(2)
<i>b</i> , Å	7.301(10)	10.832(2)
<i>c</i> , Å	12.598(3)	12.493(2)
β, °	91.76(4)	100.26(3)
Volume, Å ³	1 224.3(4)	1 185.9(4)
<i>Z</i>	4	4
Density (calculated), Mg m ⁻³	1.531	1.362
Absorption coefficient, mm ⁻¹	4.716	0.793
<i>F</i> (000)	576	512
Crystal size, mm	1.15 × 0.3 × 0.05	0.25 × 0.5 × 0.1
θ range for data collection, °	3.32–79.6	5.44–79.22
Index ranges <i>hkl</i>	–10→16, –1→8, –16→10	0→10, 0→12, –14→14
Reflections collected	2 930	2 570
Independent reflections [<i>R</i> (int)]	2 338 [0.0724]	2 402 [0.0962]
Refinement method	full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	2 330/0/179	2 401/0/183
Goodness-of-fit on <i>F</i> ²	1.023	1.025
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0714, 0.2214	0.0556, 0.1462
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0851, 0.2583	0.0881, 0.1768
Extinction coefficient	0.0000(9)	0.0043(11)
Absorption correction: empirical,		
<i>T</i> (min)	0.94	–
<i>T</i> (max)	1.08	–
Largest difference peak, Å ⁻³	0.845	0.209
hole, eÅ ⁻³	–0.648	0.290

TABLE II
Selected geometric parameters

Bond lengths, angles	1	2
O1-C2	1.325(4)	1.337(2)
C2-C1	1.416(4)	1.402(3)
C1-C7	1.446(4)	1.454(3)
C7-N1	1.295(4)	1.296(3)
N1-O2	1.313(4)	–
N1-O3	–	1.317(2)
O1-H1	1.052(42)	–
H1...O2	1.383(42)	–
O1...O2	2.425(5)	–
O1-H1-O2	170.1(3)	–
O1-H1	–	0.994(35)
H1...O3	–	1.486(35)
O1...O3	–	2.461(2)
O1-H1-O3	–	165.6(3)

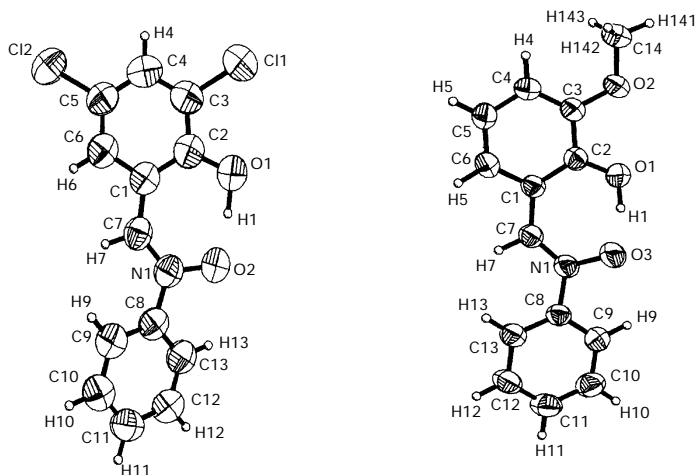


FIG. 2

ORTEP scheme and atom numbering of two independent molecules of *N*-(3,5-dichloro-2-hydroxybenzylidene)- (1) and *N*-(2-hydroxy-3-methoxybenzylidene)aniline (2) oxides

labelling of atoms are given in Fig. 2. Table II presents selected geometric parameters of the title molecules. Crystallographic data for the structures **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 135065 (**1**) and CCDC 135066 (**2**).

Compounds **1** and **2** were obtained as it is described in ref.¹⁵

RESULTS AND DISCUSSION

The spacer (bold lines in Fig. 1) is built up of six heavy atoms and consists of five bonds between the atoms in sp^2 state of hybridization: two C–C, C–N, N–O, and C–O bonds. To study the delocalisation of π -electrons in the spacer, we have enriched our own data for the title compounds (**1** and **2**, Fig. 2) by those retrieved from CSD (ref.⁹). Thus the total number of precise molecular geometries in this study rose up to 7 (with precision $AS = 1$ i.e. esd for bond lengths less than or equal to 0.005 Å). As a measure of delocalisation, we have applied the HOMA index¹⁶ accessible directly from experimental bond lengths:

$$\text{HOMA} = 1 - \alpha(R_{\text{opt}} - R_{\text{av}})^2 - (\alpha/n)\Sigma(R_{\text{av}} - R_i)^2, \quad (1)$$

where n is the number of bonds taken into the summation and α is an empirical constant fixed to give $\text{HOMA} = 0$ for the hypothetical Kekule structures of aromatic systems (with bond lengths as in acyclic polyene), and unity for the system with all bonds equal to the optimal value R_{opt} . R_{av} stands for the average bond length, while the individual bond lengths are denoted by R_i . Table III comprises empirical constants used in Eq. (1).

TABLE III
Empirical parameters used in the HOMA model¹⁶

Bonds	$R(s)$	$R(d)$	R_{opt}	α
C–C	1.467	1.349	1.388	257.7
C–N	1.465	1.269	1.334	93.52
C–O	1.367	1.217	1.265	157.38
N–O	1.415	1.164	1.249	57.21

When the HOMA model is applied to the sample of this study, the observed variation in the π -electron delocalisation in the spacer is considerable, ranging between 0.2 and 0.6 as shown in Table IV.

This observation is similar to that found for the five-membered spacers in Schiff bases with the OH...N bridge where it was shown¹ that the main factor determining the delocalisation was the substituent effect¹. Similarly to a former report¹, the weights computed *via* the HOSE model¹⁷ from the molecular geometry indicate some contribution to the canonical structure with a complete charge transfer (C) accounting for *ca* 18%, as compared with *ca* 19% for the whole sample (7 entries). Figure 3 presents the results.

The most remarkable difference between the six-membered and five-membered spacers is a much stronger H-bonding in the first type of

TABLE IV

Values of aromaticity indices (HOMA, EN, and GEO) and H-bonding energies (in kJ/mol) named EHB for systems studied. The CSD retrieved structures (1–5) have mean estimated standard deviations less than 0.005 Å

No.	REFCODE	RFAC	HOMA	EN	GEO	EHB
1	TAFRUN	0.037	0.4384	0.2609	0.300	-64.77
2	VEZSUO	0.032	0.1994	0.5662	0.234	-61.16
3	WAHZUA	0.045	0.1994	0.5122	0.288	-70.52
4	WAHZUA	0.045	0.2774	0.5449	0.177	-82.11
5	YOMYII	0.048	0.4998	0.2549	0.245	-25.36
6	1^a	0.071	0.5947	0.2055	0.199	-93.81
7	2^a	0.055	0.5247	0.286	0.256	-63.04

^a This paper, Table I.

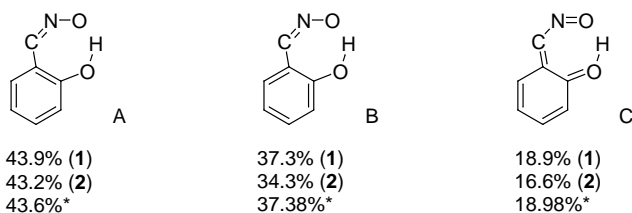


FIG. 3

Canonical structures for the title compounds and mean values for the sample of six-membered spacers (* in sample, mean value)

rings. Application of the recently modified¹⁸ Lippincott–Schroeder¹⁹ potential enabling computing the H-bond energy (EHB) from geometric parameters lead to the mean value of EHB = -69.41 kJ/mol, as compared with the value of *ca* -5.98 kJ/mol for the five-membered quasi-rings with O–H...O bonds.

If the π -electron delocalisation in the spacer depends on the H-bond strength, a relation could be expected between the strength of the H-bond measured by the H-bond energy and the delocalisation of π -electrons in the spacer estimated by HOMA. Comparison of the HOMA values and the Lippincott–Schroeder H-bond energy presented in Table IV shows that no successful correlation between the delocalisation of π -electron in the spacer and H-bond strength is observed, as shown in Fig. 4.

A similar situation is in five-membered quasi-rings, which is shown in Fig. 5 (ref.¹).

This lack of correlation in both sets of the data can serve as an argument that the H-bond interactions do not affect the π -electron delocalisation in the spacer.

Quasi-Aromaticity – Does it Exist in H-Bonded Systems?

Calvin and Wilson²⁰ suggested that the metal atom played a part in a cyclic conjugated system **4** in these β -diketone complexes thus contributed to their stability (Fig. 6).

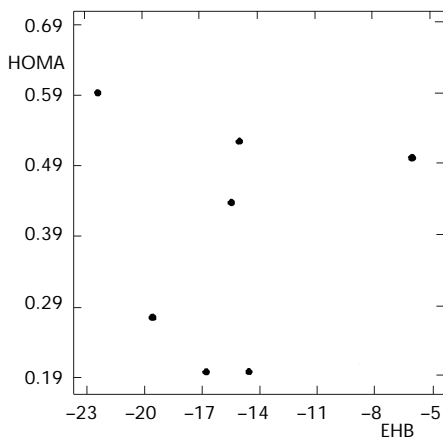


FIG. 4
HOMA vs EHB (kcal/mol, 1 kcal = 4.24 kJ) plot for 7 data points, correlation coefficient is 0.047

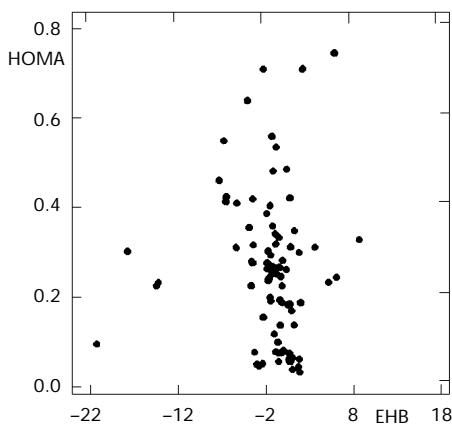


FIG. 5
Plot of HOMA values versus EHB (kcal/mol, 1 kcal = 4.24 kJ) for five-membered rings

This property was related to the term – quasi-aromaticity⁷. Does the problem arise if the H-bridge can play a similar role? Recent studies¹ showed the lack of relation between the H-bond energy and the delocalisation of π -electrons in the spacer¹. However, due to a shorter length of the spacer, strain has weakened the H-bonding and this effect could obscure a potential relationship between the energy and delocalisation. However, the results of the present report are in line with the results presented earlier in spite of a stronger H-bonding. To consider this problem from an independent point of view, we have undertaken calculations on model systems applying Schleyer's NICS values aromaticity index defined as the absolute magnetic shieldings computed at (in this case) quasi-ring centers²¹.

Figure 7 presents HOMA and NICS for three conformations of the model system with intramolecular H-bonding. Geometry optimizations have been performed by use of B3LYP/6-311+G** schemes of calculations, of NICS values at HF/6-31+G*. A conclusion may be drawn that quasi-aromaticity in the quasi-ring is negligible. The aromatic systems have negative NICS (*e.g.* for benzene -9.7) as compared with the anti-aromatic pentalene with NICS = $+18.1$ (ref.²¹). Thus the NICS values for the above model systems being small but positive indicate lack of aromaticity. In other words, no ring current appears in these cases. The HOMA values which measure π -electron delocalisation are relatively high due to the mesomeric effects between H donor group (which is electron-donor) and H acceptor group (which is also electron accepting) and are either independent or only partly dependent of H-bond strength^{22,23}. When the same kind of calculations was performed



FIG. 6

The localised (3) and delocalised (4) structures formed by metal-complex of β -ketone

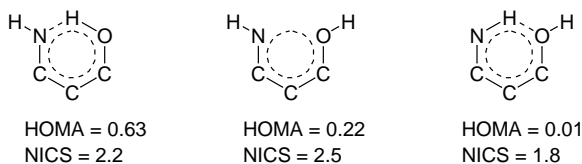


FIG. 7

HOMA and NICS values for three conformers of the model system

for a model system in which proton in the H-bond was replaced by Li^+ , the values of HOMA = 0.945, and NICS = -1.79. Thus by chelating Li^+ , the π -electron quasi-ring becomes more aromatic than in the case of the H-bonded system.

The conclusion may be drawn, that for the metal-chelating systems, the term quasi-aromaticity might be in use, whereas in the case of H-bonded systems, the use of this term seems inadequate.

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