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π-Electron Delocalisation in the Spacer of the O-H...N Bridge in Schiff Bases. Crystal and Molecular Structure of 3,5-dimethoxy-2 [(phenylimino) methyl]phenol and 4-methoxy-2-[(phenylimino) methyl] phenol.

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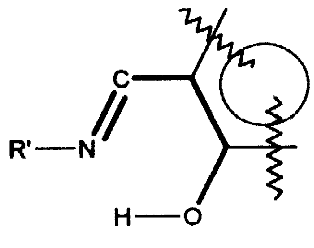
Abstract The spacer built up of N=C, two CC, and CO bonds between the H-bond donating OH group and H-bond accepting nitrogen atom in the C=N bond in Schiff bases exhibits a significant and strongly diversified degree of the π-electron delocalisation. No dependence between the delocalisation of π electrons and the H-bond strength is observed. The most important factor appears to be the mesomeric effect of the substituents attached to the ring of which a bond is a part of the spacer. This is supported by analysis of the geometry of 3,5-dimethoxy-2[(phenylimino) methyl] phenol and 4-methoxy-2-[(phenylimino) methyl] phenol presented in this study and molecular geometries of 47 well solved X-ray structures retrieved from the CSD. © 1999 Elsevier Science Ltd. All rights reserved.

Introduction

Schiff bases represent a very interesting group of compounds for studying H-bond properties.[1-5] Much less is known about the π-electron structure of the heavy atom part of the ring, i.e. the skeleton building up the spacer between the H-bond donor and acceptor, that is drawn in bold lines in scheme I.

Scheme I.



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This part of the molecule might be considered as a quasiaromatic one[6,7] and the question arises how far the π-electron delocalisation in this fragment depends on the strength of the H-bond or on the other factors operating in the molecule or in the molecules in the crystal lattice.

The aim of this report is to consider this problem taking into account our own X-ray results on the molecular geometry of 3,5-dimethoxy-2[(phenylimino)methyl]phenol (I), and 4-methoxy-2-[(phenylimino)methyl]phenol (II), (Fig. 1) and extending this data for the analogous derivatives retrieved from the Cambridge Structural Database.[8]

Experimental

The Schiff bases (I) and (II) were prepared by the reaction of the suitable aldehydes with amines in ethanol by the standard procedure, then purified by recristallisation from hexane and verified by NMR specroscopy. M.p. for (I) 96-97° C, for (II) 70-71° C.

Table 1. Crystal data and structure refinement for 3,5-dimethoxy-2[(phenylimino) methyl]phenol (I) and 4-methoxy-2-[(phenylimino) methyl] phenol (II).

Compound	I	II
Empirical formula	$C_{15}H_{15}NO_3$	$C_{15}H_{15}NO_2$
Formula weight	257.28	241.28
Temperature	293(2) K	
Wavelength	1.54178 A	
Crystal system	Monoclinic	Monoclinic
Space group	Pc	$P2_1/c$
Unit cell dimensions	a = 10.529(2) A b = 9.718(2) A c = 12.736(3) A β = 100.63(3)°	a = 13.116(3) b = 9.197(2) A c = 10.543(2) A β = 97.70(3)°
Volume	1280.8(5)A^3	1260.3(5) A^3
Z	4	4
Density (calculated)	1.334 Mg/m^3	1.272 Mg/m^3
Absorption coefficient	0.763 mm^{-1}	0.679 mm^{-1}
F(000)	512	544
Crystal size	0.25 x 0.5 x 0.1 mm	0.2 x 0.1 x 0.4 mm
Theta range for data collection	4.27 to 79.27 deg.	3.40 to 79.19 deg.
Index ranges	-13<=h<=13 0<=k<=12 -15<=l<=15	-14<=h<=13, -11<=k<=1, -1<=l<=12
Reflections collected	5350	3181
Independent reflections	5350 [R(int) = 0.0000]	2427 [R(int) = 0.0461]
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5340 / 2 / 377	2426 / 0 / 185
Goodness-of-fit on F^2	1.073	0.996
Final R indices [I>2sigma(I)]	R1 = 0.0496 wR2 = 0.1232	R1 = 0.0454 wR2 = 0.1052
R indices (all data)	R1 = 0.565 wR2 = 0.1388	R1 = 0.1625, wR2 = 0.1561
Extinction coefficient	604(53)	0.024(2)
Largest diff. peak and hole	0.258 and -0.294 e.A^{-3}	0.252 and -0.200 e.A^{-3}

The X-ray measurements of monocrystals of 3,5-dimethoxy-2[(phenylimino) methyl] phenol and 4-methoxy-2-[(phenylimino) methyl] phenol were carried out on a KM-4 KUMA diffractometer with graphite monochromated CuKα radiation. The data was collected at room temperature using the ω-2θ scan technique. The intensity of the control reflections varied by less than 3%, and the linear correction factor was applied to account for this effect. The data was also corrected for Lorenz and polarisation effects, but no absorption correction was applied. The structure was solved by direct methods[9] and refined using SHELXL.[10] The refinement was based on F^2 for all reflections except those with very negative F^2. 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 H-atoms were placed in the calculated positions, and their thermal parameters were refined isotropically. The atomic scattering factors were taken from the International Tables.[11] Details of the X-ray measurements and crystal data for both title compounds are given in Table 1, whereas the ORTEP schemes and labelling of atoms are given in Fig 1.

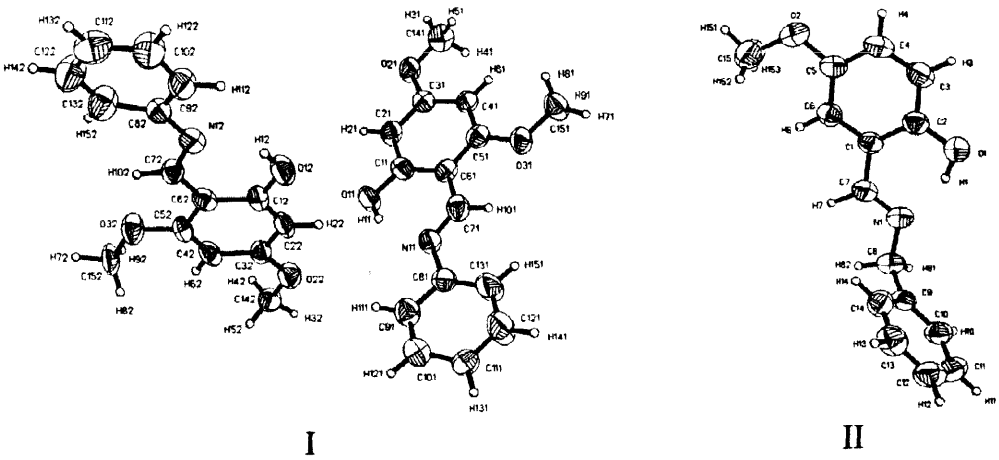


Fig. 1. ORTEP scheme and atom numbering of two independent molecules of 3,5-dimethoxy-2[(phenylimino) methyl] phenol (I) and of 4-methoxy-2-[(phenylimino) methyl] phenol (II).

Results and Discussion

The spacer built up of five heavy atoms (bold lines in scheme I) consists of four bonds between atoms in sp^2 state of hybridization: two CC-, CN- and CO-bonds. To study the delocalisation of π-electrons in the spacer we have retrieved from the CSD[8] all the available molecular geometries for systems with the same spacer as that in the title compounds (cf. scheme I). The number obtained was 47 structures of AS=1 precision[8] (esd for bond lengths less than 0.005A). As a measure of delocalisation we have applied HOMA index[12] which is a well-known and widely tested index of aromaticity based directly on bond lengths:

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

where n is the number of bonds taken into the summation and α is an empirical constant fixed to give HOMA = 0 for the hypothetical Kekule structures of aromatic systems (with bond lengths as in an acyclic polyene), and HOMA = 1 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 depicted by R_i. Table 2 presents the applied constants used in equation 1, whereas 3 gathers the data which are subject of further analysis.

Table 2 Empirical parameters used in the HOMA model.[12]

	R(s)	R(d)	R_{opt}	α
CC	1.467	1.349	1.388	257.7
CN	1.465	1.269	1.334	93.52
CO	1.367	1.217	1.265	157.38

*) This paper

The distribution of the HOMA values for this sample is presented in Fig 2.

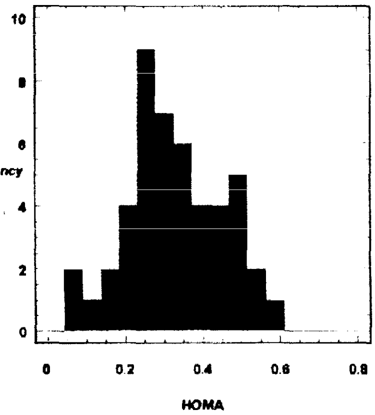


Fig. 2 Distribution of HOMA values estimated for bonds in the spacer of 47 Schiff bases.

It is immediately clear that the variation in the π-electron delocalisation in the spacer measured by the HOMA index is considerable, ranging between 0.05 - 0.65. In principle the electronic structure, and hence the lengths of these bonds, may be influenced by four effects:

(i) push-pull effects between the electron-donating hydroxy group and electron-accepting nitrogen of the C=N bond (typical substituent effects); [13]

(ii) H-bond formation which can rearrange the electronic structure of the above-mentioned atoms leading to consequences in the spacer,[14,15]

(iii) the whole above mentioned π-electron system may be affected by the substituent effects[16] from the ring being part of the given molecule of Schiff base and

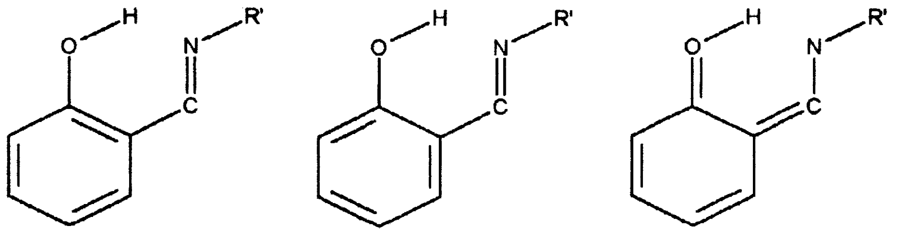
(iv) the N..O interatomic distance, strongly influencing the strength of O-H..N interactions is also the subject of crystal lattice forces, which may modify this distance easily, since opening (or closing) the angles between the bonds requires less energy than stretching or lengthening of bonds.[17]

Table 3 Aromaticity indices of the Schiff bases studied in this paper.

REFCODE	*RFAC	HOMA	EN	GEO
1 BANGOM01	0.039	0.3599	0.2683	0.3717
2 BAXJUF	0.048	0.2766	0.1888	0.5346
3 CEBKEZ	0.050	0.5051	0.1912	0.3037
4 CIWWAG	0.046	0.3400	0.2689	0.3910
5 CULPOO	0.046	0.4153	0.2218	0.3628
6 GERPEY	0.047	0.3188	0.3304	0.3508
7 GERPEY01	0.049	0.2477	0.3784	0.3739
8 GEXKID	0.043	0.3111	0.2343	0.4547
9 GEYRAD	0.042	0.1148	0.3991	0.4861
10 GIMBUZ	0.039	0.3335	0.2237	0.4428
11 GIMBUZ	0.039	0.4798	0.1750	0.3452
12 GIMBUZ01	0.036	0.3212	0.2134	0.4655
13 GIMBUZ01	0.036	0.3072	0.2107	0.4821
14 HEGHUW	0.038	0.3566	0.2794	0.3640
15 HEGJAE	0.043	0.2225	0.3734	0.4041
16 HELBOP	0.044	0.0729	0.4065	0.5206
17 HELBOP	0.044	0.0620	0.3639	0.5741
18 JEYCAR	0.042	0.2035	0.3765	0.4200
19 KASZAF01	0.047	0.2822	0.2986	0.4192
20 KUFVEM	0.044	0.2906	0.4045	0.3050
21 SANYIP01	0.048	0.3742	0.2693	0.3565
22 SUFCAX	0.035	0.2428	0.3969	0.3603
23 TAKREC	0.035	0.4535	0.1671	0.3793
24 TELKEA	0.038	0.1793	0.3886	0.4321
25 VEBREZ	0.036	0.3142	0.3052	0.3806
26 WEHFEU	0.029	0.3798	0.1912	0.4290
27 YICNUT	0.039	0.5140	0.1635	0.3225
28 YICPAB	0.029	0.4883	0.1519	0.3598
29 YODHEE01	0.038	0.2147	0.3019	0.4834
30 YORFIU	0.029	0.4610	0.1692	0.3699
31 YOXGAT	0.039	0.4365	0.1575	0.4060
32 ZAMLUU	0.037	0.5914	0.1560	0.2526
33 ZAMZUI	0.041	0.3886	0.1536	0.4577
34 ZEHHUP	0.046	0.2717	0.4078	0.3205
35 ZEVTUP	0.031	0.1423	0.2773	0.5804
36 ZEXYOQ	0.047	0.4502	0.3228	0.2270
37 ZIKNOW	0.041	0.2491	0.2163	0.5347
38 ZIVFIT	0.038	0.4720	0.1670	0.3610
39 ZIVFIT	0.038	0.2727	0.1335	0.5938
40 ZOPYAE	0.033	0.2448	0.2586	0.4967
41 ZUHSUQ	0.044	0.3792	0.2164	0.4044
42 ZUHSUQ	0.044	0.3590	0.1889	0.4520
43 ZUHSUR	0.045	0.2237	0.2916	0.4847
44 ZUHSUR	0.045	0.2904	0.2843	0.4253
45 Ia*	0.049	0.5454	0.0887	0.3659
46 Ib*	0.049	0.5387	0.2162	0.2451
47 II*	0.045	0.2685	0.2232	0.5083

The push-pull effect (i) is associated with H-bond formation (ii) and is in line with it since the intramolecular charge transfer from the hydroxy group to the amino group will lead to the strengthening of the H-bond.[14,15] If this effect is strong, it should be observed as large values of the weights of canonical structure in which the charge is transferred from the hydroxy group to the nitrogen atom in C=N (canonical structure C in scheme II). These weights may be computed via HOSE model[18] from the molecular geometry. Scheme II presents the results.

Scheme II



44.02% (I,1) 43.28% (I,2) 49.41% (II)	42.05% (I,1) 37.83% (I,2) 38.42% (II)	13.93% (I,1) 18.88% (I,2) 12.18% (II)
(A)	(B)	(C)

The weights of the canonical structure with a complete charge transfer (C) is low in all three cases, between 12 and 19%, indicating a rather small effect of this kind.. Moreover, if the π-electron delocalisation in the spacer depends on the H-bond strength one could expect at least a rough relation between the O...N interatomic distance in the H-bond and the delocalisation of π-electrons in the spacer. No such correlation is observed, as shown in Fig. 3.

Since the H-bond strength depends on the interatomic O..N distance, which in turn may be relatively easily deformed by crystal lattice forces this lack of correlation means that effect (iv) may be neglected.

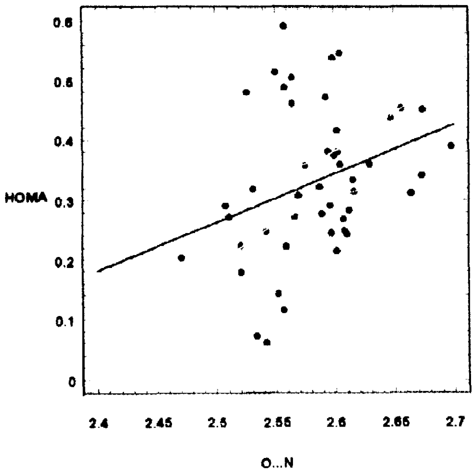


Fig. 3 Scatter - plot of HOMA values vs O...N interatomic distance (in A).

In view of these results it seems that the most important factor affecting the π-electron delocalisation in the spacer is the substituent effect from substituents attached to the ring of which the bond is the part of the spacer. In the case of compound (I) two electron-donating methoxy groups are in positions *ortho* and *para* to the C=N substituent and hence a substantial mesomeric effects may appear. As a result there is a smaller difference between the percent value of canonical structures (A) and (B) and the higher HOMA value for compound I (HOMA >0.5 for both structures of I). In the case of compound II the methoxy group is in the *meta*-position to the C=N group, and hence the mesomeric effect is much smaller and in consequence there is a much stronger bond alternation in the ring, HOMA about 0.25. To draw a still stronger conclusion, we have separated the CSD-sample into two groups: one, in which the ring consisting of the bond belonging to the spacer is substituted (sample S) and the other one, in which that ring was not substituted (sample NS). Calculation of the mean HOMA values for those two samples allowed us to answer the question: does the substituent effect in the ring influence the delocalisation in the spacer ? The HOMA value for sample S is 0.371 whereas for NS it is 0.287. If the substituents in the ring are located in *para* or *ortho* positions related to the hydroxy and the imino groups, and substituents are electron-accepting and electron-donating, respectively, then the effect on the π-electron delocalisation in the spacer should be still greater. Indeed, the subsample consisting of 5 bases with substituents strongly interacting with OH or C=N groups has a large HOMA value = 0.506. Thus the conclusion is that **the substituent effect in the ring consisting of the bond belonging to the spacer exerts a substantial effect on the delocalisation of π-electrons in the spacer. This effect is particularly large if the substituents may interact mesomerically with either the oxygen atom of the OH group or with the C=N group.** This conclusion may be nicely supported by the results of a detailed study of another Schiff base with strong mesomeric interactions[5] in which it was shown that the substituent effect could even lead to substantial changes in H-bond structure. In our cases these interactions are too weak to affect the H-bond which is also under the influence of other factors.

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