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Angular group induced bond alternation (AGIBA). Part VI — Competition between the AGIBA and through resonance effects†

Edyta Pindelska, Tadeusz M. Krygowski,* Romana Anulewicz-Ostrowska, Michal K. Cyrański and Jacek Nowacki

Department of Chemistry, University of Warsaw, Pasteura 1, 02 923 Warsaw, Poland

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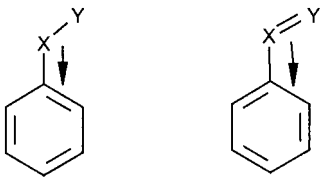
ABSTRACT: Analysis of the molecular geometry of three experimental model compounds, 2,3-dimethyl-*p*-anisaldehyde, 2,5-dimethyl-*p*-anisaldoxime and 2,3-dimethyl-*p*-anisaldoxime, and eight compounds (*p*-nitrosoaniline, *p*-nitroanisole and two conformers each of *p*-nitrosoanisole, *p*-anisaldehyde and *p*-anisaldimide) whose molecular geometry was obtained by optimization at the B3LYP/6–311G** level of theory, where both the AGIBA and through resonance effects were present, led to the conclusion that the competition between these effects does not reduce any of them significantly. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: substituent effect; AGIBA effect; *ab initio* DFT; x-ray

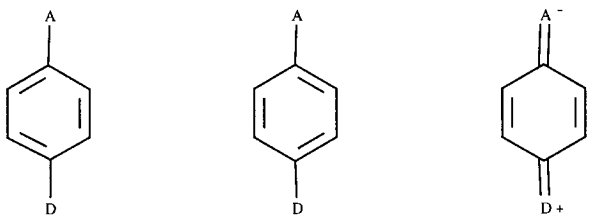
INTRODUCTION

Angular groups substituted on monocyclic π-electron systems cause substantial structural consequences[1–4] known as angular group induced bond alternation (AGIBA).[5–7] These effects are illustrated in Scheme 1: the single- and double-bonded groups cause a shortening and a lengthening, respectively, of the *cis*-CC bond in the benzene ring.



Scheme 1

The local structural changes are then propagated over the whole aromatic rings such as benzene or *s*-triazine and even non-aromatic rings such as borazine and boraxine.[8,9] However, in many cases the π-electron ring may be substituted by various groups which in addition to the AGIBA-like interactions also exhibit the usual electronic effects, which may be typically described by the Hammett substituent constants, σ.[10] In the case of a through resonance between the substituent and the group in question (often named the reaction site), their modifications, σ^+ or σ^-, have to be used (for reviews, see Ref. 11). A typical representation of these two kinds of substituent effects may be given by canonical structures K1, K2 and Q as shown in Scheme 2, where D and A denote the electron-donating and accepting substituents, respectively.



Scheme 2

For weakly interacting A and D substituents, the weight of the canonical structure Q is low. It increases when through resonance operates in a system, as it was observed, e.g., in VB computations for *p*-nitrophenol and *p*-nitroaniline.[12] A similar picture[13] was also found for these cases if the empirical model HOSE[14] was applied. The AGIBA effect leads to a substantial imbalance of the weights of K1 and K2, whereas the through resonance causes an increase of the weight of Q. The consequences of the joint action of the two effects are unknown. Some preliminary results have been obtained in this regard by

**Correspondence to:* T. M. Krygowski, Department of Chemistry, University of Warsaw, Pasteura 1, 02 093 Warsaw, Poland.
E-mail: tmkryg@chem.uw.edu.pl
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Table 1. Crystal data and structure refinement of 2,3-dimethyl-*p*-anisaldehyde (**1**), 2,5-dimethyl-*p*-anisaldoxime (**2**) and 2,3-dimethyl-*p*-anisaldoxime (**3**)

	1	**2**	**3**
Empirical formula	$C_{10}H_{12}O_2$	$C_{10}H_{13}NO_2$	$C_{10}H_{13}NO_2$
Formula weight	164.20	179.21	179.21
Temperature (K)	293(2)	293(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Triclinic, P-1
Unit cell dimensions	$a = 7.1480(10)$ Å	$a = 6.8400(14)$ Å	$a = 7.4494(15)$ Å
	$b = 8.039(2)$ Å	$b = 8.0100(16)$ Å	$b = 7.7594(16)$ Å
	$c = 15.257(3)$ Å	$c = 17.800(4)$ Å	$c = 9.0504(18)$ Å
	$\alpha = 90.0°$	$\alpha = 90.0°$	$\alpha = 82.64(3)°$
	$\beta = 102.39(3)°$	$\beta = 99.00(3)°$	$\beta = 69.10(3)°$
	$\gamma = 90.0°$	$\gamma = 90.0°$	$\gamma = 70.59(3)°$
Volume, V (Å^3)	856.3(3)	963.2(3)	460.9(2)
Z	4	4	2
Calculated density (mg m^{-3})	1.274	1.236	1.291
Absorption coefficient (mm^{-1})	0.088	0.086	0.090
F(000)	352	384	192
Crystal size (mm)	$0.2 \times 0.2 \times 0.25$	$0.2 \times 0.22 \times 0.25$	$0.25 \times 0.25 \times 0.3$
Theta range for data (°) collection	3.87–22.48	3.44–19.99	3.45–20.00
Index ranges	$-9 \le h \le 9$,	$-6 \le h \le 6$,	$-7 \le h \le 7$,
	$-10 \le k \le 10$,	$-7 \le k \le 7$,	$-7 \le k \le 7$,
	$-20 \le l \le 20$	$-17 \le l \le 17$	$-8 \le l \le 8$
Reflections collected/unique	10540/1120	8895/896	4362/851
	[R(int) = 0.0462]	[R(int) = 0.0730]	[R(int) = 0.0350]
Refinement method		Full-matrix least-squares on F^2	
Data/restraints/parameters	1119/0/158	896/0/171	851/0/171
Goodness-of-fit on F^2	1.050	1.083	1.092
Final R indices [I >2sigma(I)]	$R1 = 0.0362$,	$R1 = 0.0537$,	$R1 = 0.0346$,
	$wR^2 = 0.0950$	$wR^2 = 0.1524$	$wR^2 = 0.0878$
R indices (all data)	$R1 = 0.0381$,	$R1 = 0.0604$,	$R1 = 0.0366$,
	$wR^2 = 0.0979$	$wR^2 = 0.1640$	$wR^2 = 0.0909$
Extinction coefficient	0.029(6)	0.013(9)	0.024(8)
Largest diff. peak and hole (e Å^{-3})	0.187 and −0.180	0.175 and −0.181	0.241 and −0.167

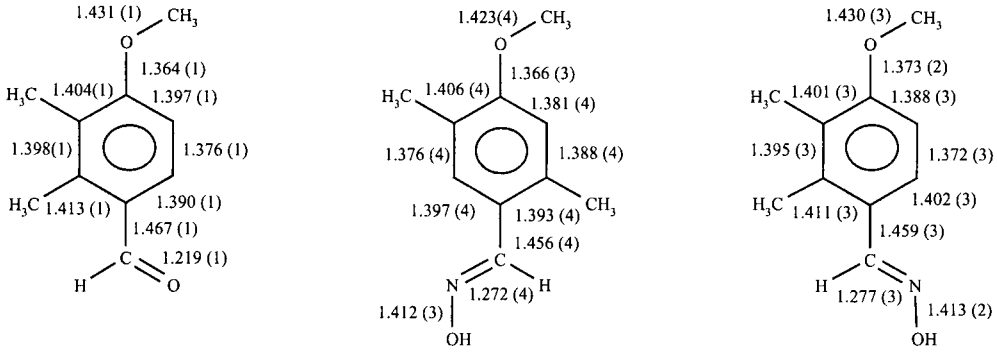
analysis of the geometry in 3,4-dimethoxybenzaldehyde(4-methylphenyl)sulphonythydrazone.[15] Depending on the conformation of the C═N group in the *para*-position to one of the two-methoxy groups, a substantial difference in imbalance between K1 and K2 appeared, while the weight of Q was practically unchanged.

The aim of this paper is to show how the competition between the AGIBA and the through resonance substituent effects can interfere with each other. In order to do so, experimental geometries of 2,3-dimethyl-*p*-anisaldehyde (**1**), 2,5-dimethyl-*p*-anisaldoxime (**2**) and 2,3-dimethyl-*p*-anisaldoxime (**3**) were determined by x-ray diffraction and in order to extend the field of study a collection of eight *p*-disubstituted benzene derivatives were optimized by *ab initio* computation at the B3LYP/6–311G** level of theory. Substituents of these systems were chosen in order to follow the AGIBA effect and to exhibit a varying scale of the through resonance effect.

EXPERIMENTAL

Preparations. For 2,3-dimethyl-*p*-anisaldehyde (**1**), a crystal of the commercially available compound (Aldrich) was used. The oximes **2** and **3** were prepared according to the general procedure[16] for conversion of aldehydes insoluble in water from 2,5-dimethyl-*p*-anisaladehyde and 2,3-dimethyl-*p*-anisaladehyde, respectively. A mixture of 0.5 g of an aldehyde, 0.5 g of hydroxylamine hydrochloride and 5 cm^3 of pyridine in 10 cm^3 of ethanol was refluxed for 0.5 h. After evaporation of the solvent the solid residue was mixed thoroughly with 5 cm^3 of water, filtered and washed on the filter with an additional portion of water. The crude product was recrystallized twice from 95% ethyl alcohol. By this method both 2,5-dimethyl-*p*-anisaldoxime (**2**) and 2,3-dimethyl-*p*-anisaldoxime (**3**) were obtained with >90% yields as colourless crystals, m.p. 137–138.5 and 116–117 °C, respectively.

Crystal structure determination. Crystal data regarding the structures of **1**–**3** are given in Table 1, together with refinement details. All measurements of the crystals were performed on a Kuma (Wrocław, Poland) KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation. The crystal was positioned at 65 mm from



1 **2** **3**

Scheme 3

the KM4CCD camera and 888 (**1**), 796 (**2**) or 708 (**3**) frames were measured at 1.5° (**1**), 1.6° (**2**) or 1.8° (**3**) intervals with a counting time of 15 s. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction programs.

The structure was solved by direct methods[17] and refined using SHELXL.[18] The refinement was based on F^2 for all reflections except those with very negative F^2. The weighted R factors wR and all goodness-of-fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $F_0^2 > 2s(F_0^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. All hydrogen atoms were located from a differential map and refined isotropically. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in Ref. 19.

Crystallographic data (excluding structural factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 161453 (**1**), CCDC 161454 (**2**) and CCDC 161452 (**3**). Copies of the data can be obtained free of charge on application to CCDC (E-mail: deposit@ccdc.cam.ac.uk).

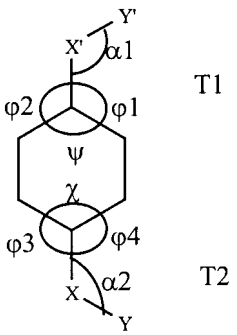
Computations. All optimizations were carried out at the B3LYP/6–311G** level of theory by use of Gaussian 94.[20]

RESULTS AND DISCUSSION

Structural deformations due to the AGIBA effects are similar to some extent to those observed for benzene rings anneleated with small rings and underlying the Mills–Nixon effects.[21] Undoubtedly one of the components operating in the AGIBA effect is that due to the rehybridization,[4–6] which is the main factor causing deformations in typical Mills–Nixon affected systems.[21,22] It is worth noting that the AGIBA effect depends clearly on the conformation of substituents;[23] on varying the conformation, say, from *cis* to *trans*, one changes the AGIBA effect from a maximum to a minimum (or conversely depending on the nature of the angular substituents), whereas the electronic substituent effects remain practically unchanged in both cases.

Experimental geometry

The molecular geometry of **1**–**3** (Scheme 3; for labelling of the geometrical parameters, see Scheme 4; for all data, see Table 2) allowed us to estimate canonical structure weights by use of the HOSE model,[14] which led to the conclusion that in two cases (**1** and **3**) when the methoxy and C=N groups act one against another in a *cis* orientation, the imbalance of $K1$ and $K2$ is small, 30.1:34.0% and 32.6:31.5%, respectively, with the highest weights for the quinoid structure, Q, 35.9 and 36.0%, respectively. In the case of **2**, where both substituents work in line, the imbalance $K1$:$K2$ becomes large (26.6:41.4) with a reduction of the Q value to 32.07%. Locally, these global effects are not so clearly observed: the *cis* bonds in the ring are always shorter for the methoxy group, but the effects due to the double bonded



Scheme 4

Table 2. Canonical structure weights and valence and torsion angles for molecules **1**, **2** and **3** (for labelling, see Scheme 4)

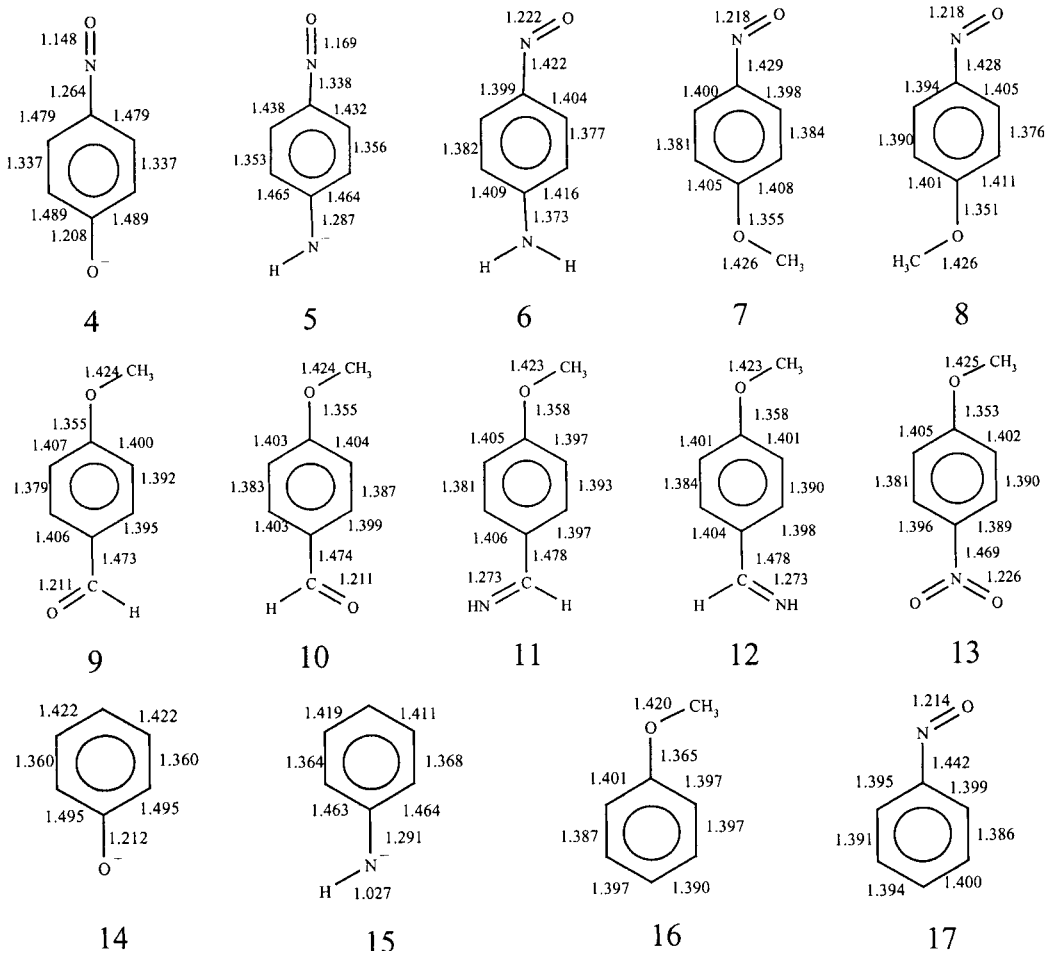
Compound	*K*1 (%)	*K*2 (%)	*Q* (%)	φ1 (°)	φ2 (°)	φ3 (°)	φ4 (°)	ψ (°)	χ (°)	α1 (°)	α2 (°)	*T*1 (°)	*T*2 (°)
1	30.14	33.98	35.88	122.9	115.7	121.9	118.3	121.3	119.8	117.6	124.2	−6.2	7.2
2	26.57	41.36	32.07	124.4	115.4	121.5	120.4	120.2	118.1	117.5	123.3	1.7	0.1
3	32.58	31.47	35.95	121.0	116.0	118.2	120.1	123.0	121.7	117.9	121.8	−4.9	−1.0

groups, C═O or C═N, are not always in line with expectations. This is probably due to a steric effect caused by the methyl group introduced in order to obtain a proper conformation. These might affect in some way the picture leading to the above-mentioned irregularities observed in the local picture. Therefore, in the next section the optimized geometry of some model molecules is subjected to deeper analysis.

If there is one angular group attached to the ring in K1 in Scheme 2, the *cis* CC bond in the ring is a single bond. If there are two such groups, and one of them is double bonded in K1, the *cis*-CC bond to this group is a single bond. All weights were calculated applying the HOSE[14] model only to the ring CC bonds.

Ab initio optimized geometry

Systematic analysis of the joint action of the through resonance and AGIBA effects was carried out in two series since two kinds of AGIBA substituents have to be taken into account: single- and double-bonded, X—Y and X═Y. As a typical angular substituent with a single bond, the methoxy group was chosen. It exhibits a large structural effect[6] and is assumed to represent only one mechanism of interactions, the rehybridization at the *ipso* carbon atom. The other kind of the angular substituents, those with a double bond, X═Y, are assumed to interact with the ring via a mechanism composed of two effects:[4,5] the rehybridization and a through space π-



Scheme 5

Table 3. Canonical structure weights and geometrical parameters optimized by B3LYP/6–311G** for molecules **4–17**, (for labelling, see Scheme 4)

Compound	*K*1 (%)	*K*2 (%)	*Q* (%)	φ1 (°)	φ2 (°)	φ3 (°)	φ4 (°)	ψ (°)	χ (°)	α1 (°)	α2 (°)	*T*1 (°)	*T*2 (°)
4	2.50	2.50	95.00	118.8	118.8	121.7	121.7	122.4	116.6	180.0	–	0.0	–
5	5.45	5.09	89.46	117.9	117.4	125.3	116.8	123.2	117.9	137.7	112.6	94.5	−0.3
6	32.08	26.78	41.14	124.2	116.2	120.7	120.2	119.7	119.0	115.7	118.4	0.0	17.6
7	30.80	31.6	37.6	123.9	115.9	117.3	122.2	120.2	120.2	115.5	109.8	0.0	0.0
8	37.80	25.64	36.56	124.1	115.8	124.5	115.2	120.1	120.2	115.5	119.1	180.0	180.0
9	37.75	26.66	35.59	124.6	115.4	120.7	120.3	120.0	119.0	118.9	125.1	180.0	180.0
10	32.98	30.46	36.56	124.4	115.6	120.0	120.6	120.0	119.0	118.9	125.1	0.0	−0.1
11	37.84	27.32	34.84	124.9	115.6	123.1	119.1	119.5	117.8	118.7	129.9	0.0	0.0
12	34.59	30.20	35.21	124.6	115.9	119.0	123.2	119.5	117.8	118.8	129.9	0.0	0.0
13	29.58	36.58	33.84	124.5	115.6	119.4	119.3	119.9	121.3	119.0	117.8	0.0	0.0
14	11.27	11.27	77.46	–	–	120.9	120.9	124.2	118.3	–	–	–	–
15	13.77	15.17	71.06	–	–	124.8	116.2	123.2	119.0	–	112.7	–	0.0
16	30.27	38.34	31.39	124.6	115.7	–	–	119.7	119.2	118.5	–	0.0	–
17	36.44	30.84	32.72	123.6	115.3	–	–	121.1	119.7	115.3	–	0.0	–

electron effect. For this group of AGIBA substituents we chose the nitroso, formyl and imino groups, which are also known as strongly electron-accepting groups. Some strong electron-donating and accepting substituents which do not cause the AGIBA effect were used as references.

Scheme 5 and Table 3 present molecular geometries and canonical structure weights for nitrosobenzene (**17**) and anisole (**16**) and their *para*-substituted derivatives.

In order to study the resonance effects in the *para* position of nitrosobenzene, derivatives with typical electron-donating groups (O^-, NH^-, NH_2, OMe) were chosen. Of those, the methoxy group was studied in two conformations with respect to the nitroso group. In the case of strongly electron-donating substituents (O^- and NH^-), for molecules **4** and **5** the nitroso group exhibits unusual behaviour as it becomes linear and not angular with a substantial shortening of the CN and NO bonds, respectively. In these cases no AGIBA effect is expected, although in the case of the angular NH^- group a slight AGIBA effect is observed just from this substituent; the imbalance is 5.45:5.09%. In the case of a weaker electron-donating substituent, the amino group (**6**), the imbalance of *K*1 and *K*2 is substantial (32.1:26.8%), indicating that the through resonance (41.1% of the *Q* structure) affects the AGIBA effect only slightly. This is supported by the value of the imbalance that resembles the case of unsubstituted nitrosobenzene (**17**), 36.4:30.8%. This similarity is even clearer if we compare the differences between *K*1 and *K*2: they are 5.3 and 5.6% for **6** and **17**, respectively. The *p*-methoxynitrosobenzene is presented in two conformations. In molecule **7** where both groups are in *cis*-positions the substituents act one against another, and the AGIBA effect may be cancelled out. The observed imbalance of the canonical structure is very small here (30.8:31.6%), in line with our expectations. For the *trans* conformer (**8**), where the AGIBA effects from both substituents sum up, the imbalance is substantial: *K*1:*K*2 = 37.8:25.6%. In both cases (**7** and **8**) the weight for *Q* is similar: 37.6 and 36.6%.

This last kind of case was studied with *para* derivatives with two angular substituents, formyl and imino groups. In both cases the *trans* conformers (**9** and **11**) exhibit a substantial and similar imbalance, 37.7:26.7% and 37.8:27.3%, respectively. Both *cis* conformers (**10** and **12**) do not exhibit clear structural trends. For all four cases (**9–12**), the weight for the quinoid structure, *Q*, is almost unchanged, between 34.8% (for **9**) and 36.6% (for **10**).

All the above results were obtained for planar or almost planar systems, with torsion angles (*T* in Table 3) below 10°, except **6**, where this angle for the amino group is greater (17.6°), owing to the known non-planar structure of the amino group.

CONCLUSION

AGIBA effects, despite their low energetic consequences,[24] are observed when competition with through resonance is present. However, the competition between these effects does not reduce any of them significantly.

Acknowledgements

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