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Angular Group-Induced Bond Alternation. III. The Case of *ortho*-Dimethoxybenzene Derivatives. Crystal and Molecular Structure of 3,4-Dimethoxybenzaldehyde (4-methylphenyl)sulfonylhydrazone

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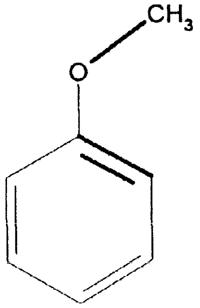
Abstract. The crystal and molecular structure of the 3,4-dimethoxybenzaldehyde (4-methylphenyl)-sulfonylhydrazone is reported, with R = 0.0647. Application of the HOSE model to the molecular geometry of the title compound, together with the most precise molecular geometries for 36 *ortho*-dimethoxy derivatives of benzene retrieved from Cambridge Structural Database (CSD) and supplemented by *ab initio* RHF/6-311G** calculations, led to the conclusion that the *o*-dimethoxy groups cause significant changes in ring geometry, fully in line with the concept of Angular Group Induced Bond Alternation (AGIBA).

INTRODUCTION

It has recently been shown[1-7] that angular substituents induce substantial bond length alternation in the ring of benzene derivatives (the "AGIBA" effect).[5] Similar structural effects have also been observed for other aromatics, e.g. for derivatives of s-triazine[4,8] and boroxine and borazine.[8] The methoxy group interacts most strongly in this manner[5,6] producing an imbalance of the Kekule structures **1** and **2** in the ratio[1] 53:47 according to the HOSE model[9] from the *ab initio* geometry calculated at HF/6-31G* [10] level of theory.



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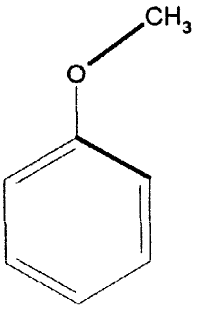

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PII: S0040-4020(98)00748-0

The AGIBA effect was also experimentally supported by a low-temperature X-ray structure determination of 1,3,5-trimethoxy-substituted benzene[2] and s-triazine,[4] and statistically verified for a sample of 20 monosubstituted diaza-derivatives of benzene.[3]

The aim of this paper is to study how two methoxy groups in *ortho* positions affect the geometry of the ring in benzene derivatives. Following the rule describing the conformational dependence of the AGIBA effect on the substitution,[2,5,11] in these cases a considerable enhancement of the effect should be observed. In order to prove it we have solved the crystal and molecular structure 3,4-dimethoxybenzaldehyde (4-methylphenyl)-sulfonylhydrazone and employed structural data for *o*-dimethoxybenzene derivatives retrieved from the CSDC.[12]

EXPERIMENTAL AND COMPUTATIONAL DETAILS

Synthesis. The title compound was prepared following the reported procedure[13] from 3,4-dimethoxybenzaldehyde and 4-toluenesulfonylhydrazine. Twofold crystallisation from methanol gave a colourless product, m.p. 139-139.5°C , yield 81%, I.R.;ν_{max} 3200, 1600, 1525, 1270, 1165, 1020, 900, 550 cm^{-1}; ^{1}H NMR δ(ppm) = 2.39 (s, 3H, 11-C$\underline{H}_3$), 3.86 (s; 3H, 1-OC$\underline{H}_3$)*, 3.87 (s; 3H, 2-OC$\underline{H}_3$)*, 6.79 (d, 1H, 3-H $^3J_{3,4}$=8.30Hz), 7.00 (dd, 1H, 4-H, $^3J_{4,3}$=8.30Hz, $^4J_{4,6}$=1.71Hz), 7.21 (d, 1H, 6-H, $^4J_{6,4}$=1.71Hz), 7.29 (d, 2H, 10-H; 12-H, $^3J_{10,9;12,13}$=8.30Hz) 7.73 (s, 1H, N$\underline{H}$), 7.78 (d, 2H, 9-H; 13-H, $^3J_{9,10;13,12}$=8.30Hz), 8.30 (s, 1H, 7-H); ^{13}C NMR δ (ppm)= 21.60(11-$\underline{C}$H$_3$), 55.92 (1-O$\underline{C}$H$_3$)*, 55.93 (2-O$\underline{C}$H$_3$)*, 108.33 (C-3), 110.56 (C-6), 126.27 (C-5), 127.94 (C-10,12), 129.66 (C-9,13), 135.33 (C-8), 144.22 (C-11), 148.48 (C-7), 149.23 (C-1)**, 151.20 (C-2)**. NMR atom numbering according to Fig 1. Assignment of the signals marked by an asterisk(s) is not certain. Anal: Calcd. for $C_{16}H_{18}N_2O_4S$: C, 57.5; H, 5.4; N, 8.4; S; 9.6. Found C, 57.6; H, 5.4; N, 8.4; S, 9.4%.

Spectra. ^{1}H and ^{13}C NMR spectra were obtained at 200 and 50 MHz, respectively, on a Unity plus -200 Varian spectrometer dissolved in deuteriochloroform with TMS as an internal standard. The I.R. spectrum was recorded on a Nicolet Magna I.R. 550 in KBr. The melting point was determined on a Boetius hot-stage microscope and was uncorrected.

X-ray measurements. The X-ray measurements of the monocrystal (Fig.1) were carried out on a KM-4 KUMA diffractometer with graphite monochromated CuKα radiation. The data were 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 were also corrected for Lorentz and polarisation effects, but no absorption correction was applied. The structure was solved by direct methods[14] and refined using SHELXL.[15] 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.[16] Details of the X-ray measurements and crystal data for the compound are given in Table 1.

Calculation details. A calculation of the optimised geometry was carried out at the *ab-initio* RHF/6-311G** level of theory, employing Gaussian 94.[10]

Table 1. Crystal data and structure refinement for 3,4-dimethoxybenzaldehyde (4-methylphenyl)sulfonylhydrazone.

Empirical formula	$C_{16}H_{18}N_2O_4S$
Formula weight	334.38
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 18.055(4) α= 90°.
	b = 4.998 (1) β= 91.61(3)°
	c = 18.235(4) Å γ= 90°
Volume	1644.9(6) $Å^3$
Z	4
Density (calculated)	1.350 Mg/m^3
Absorption coefficient	1.941 mm^{-1}
F(000)	704
Crystal size	0.17×0.25×0.55 mm
Theta range for data collection	3.40 to 79.41 deg.
Index ranges	-19<=h<=1, -6<=k<=1, -21<=l<=21
Reflections collected	4336
Independent reflections	3247 [R(int) = 0.1129]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3226 / 0 / 227
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0647, wR2 = 0.1608
R indices (all data)	R1 = 0.1080, wR2 = 0.2392
Extinction coefficient	0.0119(14)
Largest diff. peak and hole	0.484 and -0.586 e.$Å^{-3}$

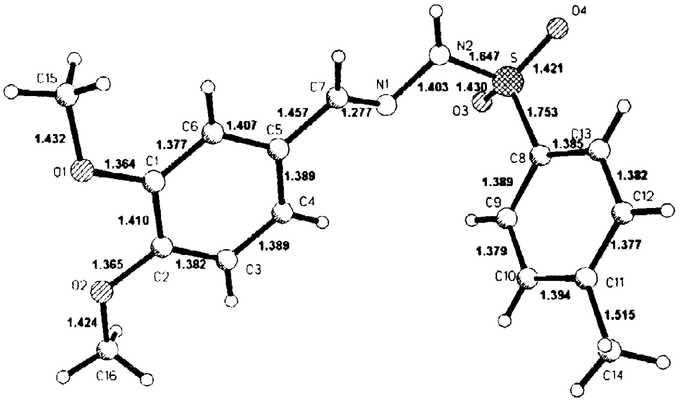

Fig. 1. Bond lengths (in Å) of 3,4-dimethoxybenzaldehyde (4-methylphenyl)sulfonylhydrazone; mean esd value is 0.003 Å.

RESULTS AND DISCUSSION

Geometry analysis of 37 *ortho*-dimethoxybenzene derivatives revealed a substantial bond length alternation in the ring. A ratio of two Kekulé structures weights (I) : (II) (Fig. 2) calculated *via* HOSE model[9] from mean geometries is 61.6:38.4, indicating a strong AGIBA effect.[1,2]

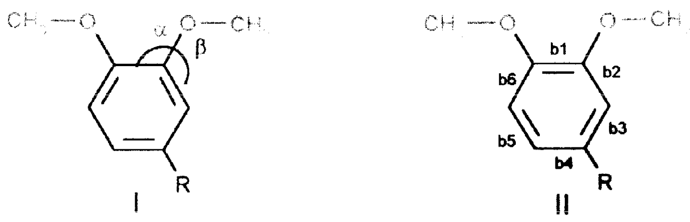

Fig 2. Canonical structures of *o*-dimethoxybenzene (R=H) and labelling of bonds and angles in question.

For comparison we have optimised the geometry of 1,2-dimethoxybenzene at *ab-initio* RHF/6-311G**[10] level of theory. The imbalance was even greater: 71.5:28.5. The lower values obtained from the mean experimental geometry of the ring may stem from the additional interactions of one of the two methoxy groups with counter substituents, which could interact *via* a through-resonance effect, and hence decrease the expected AGIBA effect. Indeed, 3,4-dimethoxybenzaldehyde (4-methylphenyl)sulfonylhydrazone is a molecule with these kind of interactions and this ratio is exactly as for the mean geometry: 61.6:38.4. In this case the observed decrease may be interpreted as a result of competition between two effects: the AGIBA effect and the through-resonance effect between *p*-methoxy and imine groups. The following interactions may be taken into account (Fig.3):

(i) two *o*-dimethoxy-groups induce an increase of the canonical structure (a),
(ii) the imine group induces an increase of the canonical structure (b), due to the action of its own AGIBA effect,
(iii) a through-resonance effect of interactions between the methoxy and imino group in *para* position induces an increase of the canonical structure (c).

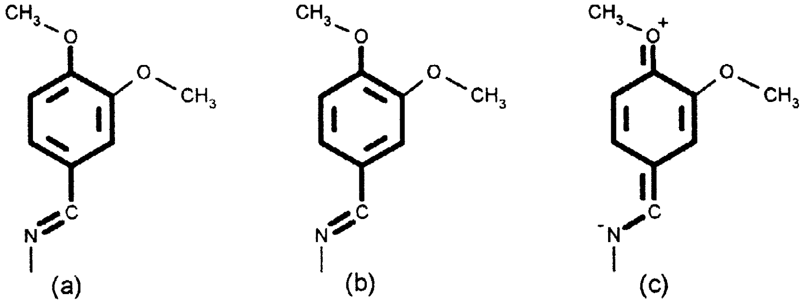

Fig 3. The canonical structures (marked in bold) describing interactions (i)-(iii).

The observed structure is a superposition of these three canonical structures, indicating action of all three effects. Application of the HOSE model[9] to the experimental geometry employing canonical structures (a) - (c) (marked in bold lines in Fig 3) gives the following weights: 50.0% for (a), 33.0% for (b) and 17.0% for (c). The obtained weights are in line with the observed bond length variation. Thus we observe that b1 and b3 are (Fig. 1, labelling Fig 2) the longest bonds in the ring; 1.410 and 1.407 Å, respectively, in line with the large weight of structures (a) and (c) in which they are assumed to be single. Similarly b2 is a double bond in these two canonical structures, and therefore it is the shortest, 1.377 Å. Bonds b4, b5 and b6 are either double or single in the canonical structures and therefore they are of a medium length between 1.382 - 1.389 Å. Fig 1 presents the bond lengths of 3,4-dimethoxybenzaldehyde (4-methylphenyl)sulfonylhydrazone, in line with the above interpretation.

The molecule of 3,4-dimethoxybenzaldehyde (4-methylphenyl)sulfonylhydrazone may exist in two conformations, of which (d) is realised in the crystalline state of the compound. In order to study deeper an interplay between the AGIBA effects stemming from both methoxy groups and from the imino group, and the through resonance between these groups, we have computed optimised molecular geometries of both conformers (d) and (e) using *ab-initio* method (RHF/6-311G**).[10]

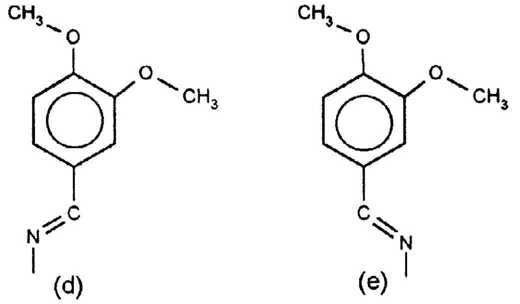

Fig. 4 Two model conformers of 3,4-dimethoxybenzaldehyde (4-methylphenyl)sulfonylhydrazone (no Kekulé structures shown)

Application of the HOSE model[9] for computing canonical structure weights revealed a great difference in AGIBA effect due to conformation of the imino group. In the case of conformer (d) the imino group acts against the AGIBA effect of two *ortho*-dimethoxy groups. In consequence the canonical structure weight for (a) is lowered to 55.5%. In the case of another conformer (e) the enhancement of AGIBA effect is observed – two dimethoxy groups and the imino group act in line leading to the canonical structure weight (a) equal to 61.3%. In both cases the canonical structure describing the through resonance effect is nearly equal: 11.2 and 10.8%, respectively.

The observed effect in experimental results for 3,4-dimethoxybenzaldehyde (4-methylphenyl)sulfonylhydrazone and the *ab initio* geometry of 1,2-dimethoxybenzene is well-supported by a statistical study of differences between the lengths of the central bond (b1) (Fig. 2) and the two adjacent ones (b2 and b6) for the set of 36 *o*-dimethoxybenzene derivatives, which is on the average 0.024 Å, significantly different from zero.

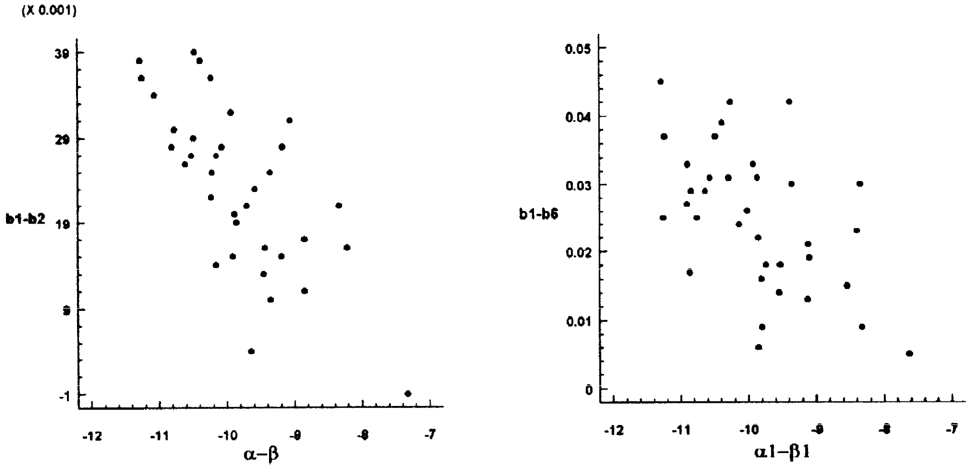

Fig 5 Scatter plots of differences in adjacent bond length (b1-b2, and b1-b6) and appropriate bond angles (α-β) and (α1-β1). Bond lengths in Å, angles in degrees.

A rough correlation between the changes of differences in bond angles (α-β) and ($\alpha 1$-$\beta 1$) and bond lengths (b_1 - b_2) and (b_1-b_6), is observed (correlation coefficients 0.70 and 0.53, respectively, Fig. 5). Both these correlations are statistically significant at the level $\alpha < 0.01$. This suggests an important contribution of the rehybridisation effect in the observed geometry changes. However, the comparison of the optimised *ab initio* geometry of *o*-dimethoxybenzene and the constrained structure with both exocyclic bond angles at substituted carbons roughly equal leads to the conclusion that the bond alternation in *o*-dimethoxybenzene is due not only to the rehybridization effect but also due to some kind of through space π-electron effects.[3]

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