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Angular-Group-Induced Bond Alternation. I. Origin Of The Effect From *Ab Initio* Calculations.

Tadeusz M. Krygowski[a] *, Marcin Wisiorowski[a],
Sean T. Howard[b] and Leszek Z. Stolarczyk[a]

[a] Department of Chemistry, University of Warsaw, ul. L. Pasteura 1, 02-093 Warsaw, Poland

[b] Department of Chemistry, University of Wales, College of Cardiff, Cardiff CF1 3TB, United Kingdom

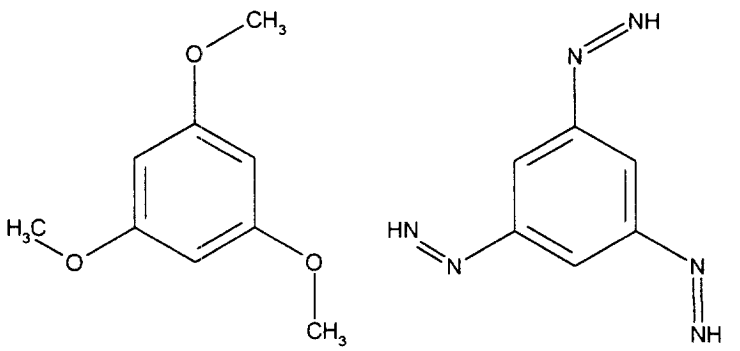
Abstract: It is shown that an angular group -XY attached to the benzene ring causes bond length alternation within the ring. This angular-group-induced bond alternation (AGIBA) effect is studied in several mono-substituted benzene derivatives by means of the *ab initio* calculations. Different alternation patterns are found for angular groups of the -X-Y and -X=Y types. The origin of the AGIBA effect is traced to a competing influence of through-space-π-electron interactions and a rehybridization effect at the substituted carbon atom. The AGIBA effect is shown to be strongly conformation dependent.

Introduction

The geometry of the phenyl ring in benzene derivatives is a subject of countless reports. The ring shape may be readily deformed in various ways from the ideal hexagon, depending on the kind of perturbation. For example, due to weak intermolecular interactions in the crystalline state, the benzene ring is no longer perfectly planar[1]. Bond-length alternation is often observed when the benzene ring is fused to one or several small rings[2-11] and is usually interpreted in terms of the Mills-Nixon effect[2]. A recent review[12] presents new synthetic achievements and theoretical calculations supporting the experimental work for preparation of benzene derivatives with a strongly localized π electron structure[13]. That kind of deformation is manifested usually by an imbalance between the weights of the two possible Kekule structures, and arises from a combination of angular strain and perturbation of the aromatic π system[6,7]. Open substituents also distort the ring geometry in a way which can create an imbalance of some canonical structures, but the kind of distortion, and hence the kind of canonical structures involved in its description, depends on the topology and the nature of the attached substituent[14]. Experimental data (IR shifts, bond lengths) for substituted benzene derivatives have been used in studies of the dependence of canonical structure contributions in the ring on the nature and position of the

substituent[14]. Theoretically calculated geometries of substituted benzene derivatives have been also used in studies of the substituent effect on the geometry of the ring[15-17].

For a conjugated π-electron system, the % content of various Kekule structures may be estimated from the bond lengths by means of the HOSE (abbreviation for Harmonic Oscillator Stabilization Energy) model[14(f),18]. In the presence of bond-length alternation in the phenyl ring, the imbalance of the two Kekule structures manifests itself by a departure from the exact 50:50 ratio. Recently, a molecular-geometry optimization of anisole[19] indicated that such an imbalance occurs under the influence of an angular substituent group - in that case the methoxy group. The imbalance of the Kekule structures became more pronounced when the C-O-Me bond angle was artificially decreased. A substantial amplification of that effect was found in the case of C_{3h} symmetry for 1,3,5-trimethoxy benzene, where the geometry optimization was performed at the HF/6-311G* level[20]. These theoretical predictions were confirmed by low-temperature X–ray determined geometries of 1,3,5-trimethoxybenzene[20] and 2,4,6-trimethoxy-*s*-triazine[21]. Apparently, the presence of the methoxy groups amplifies the Kekule structure in which the double bonds are *cis* with respect to the O-Me bonds, cf. Fig. 1a. For another angular substituent, the diaza group, the experimental geometries of 21 diazabenzene derivatives[22] indicate the opposite pattern of bond alternation within the phenyl ring, which is exemplified by 1,3,5-tris-(diazene)-benzene[22], in Fig. 1b.



70.2% 66.5%

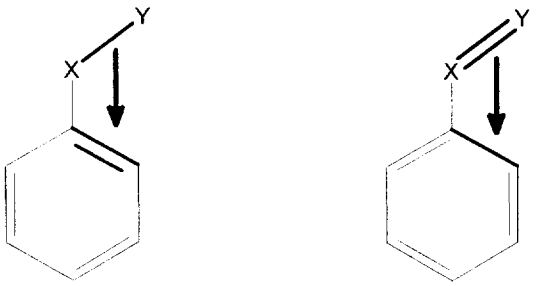
(*a*) (*b*)

Fig. 1. The dominant Kekule structures and their weights for: (*a*) 1,3,5-trimetoxybenzene[20], (*b*) 1,3,5-tris-(diazene)-benzene[21].

On the basis of experimental and theoretical geometries of several diaza-, methoxy-, and formylo-derivatives of benzene the following phenomenolgical rule was suggested[20]:

An angular substituent group of the form -X-Y (-X=Y) induces bond alternation within the phenyl ring, corresponding to an enhanced double-bond (single-bond) character of the adjacent C-C bond cis to the group.

This rule-of-the-thumb is illustrated in Fig. 2. An angular group may be also characterized by the π-electron count: assuming that each of the centers X and Y supplies a single π type-orbital which may be occupied by 0, 1, or 2 electrons, one finds that the -X-Y group corresponds to 4 π electrons, whereas the -X=Y group - to 2 π electrons. By looking at an angular group as forming an "almost closed" ring, the π-electron count may provide a link with some observations made by Baldridge and Siegel[10] for the case of annealed benzenes.



(*a*) (*b*)

Figure 2. Bond alternation pattern induced by: (*a*) -X-Y group, (*b*) -X=Y group.

The above rule summarizes our proposal for a new substituent effect[20], the angular group-induced bond alternation effect, which will be hereafter abbreviated as the AGIBA effect.

Till now, the AGIBA effect has been observed for a few angular substituent groups: methoxy-[19,20], diazo-[22], nitroso-[23] and formylo-[20] derivatives of benzene, methoxy derivative of s-triazine[21], and could be found also in triethyl derivatives of boraxin, borazine, benzene and triazine[24]. The main purpose of this paper is to clarify the origin of the AGIBA effect by exploring, at the level of the Hartree-Fock (HF) model, how it operates within a wider range of mono-substituted benzenes. It will be shown that the AGIBA effect is caused mainly by a through-space interaction of the π electrons of the -X-Y (or -X=Y) group with those of the phenyl ring. However, the presence of an angular substituent usually creates some strain in the σ-electron skeleton, which may also contribute to the observed bond length alternation.

Statistical evidence for the AGIBA effect in mono-substituted benzenes

The geometric structure of a mono-substituted benzene is depicted in Fig. 3, where the numbering of the carbon atoms and the carbon-carbon bonds within the phenyl ring, and the labelling for the exocyxlic valence angles used throughout the present paper are also given.

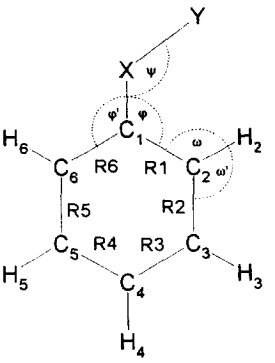


Figure 3. Molecular parameters pertinent to the discussion of the AGIBA effect.

In order to have a well-grounded opinion on the AGIBA effect in mono-substituted benzenes, we have carried out[25] HF/6-31G* calculations with full optimization of the molecular geometry for eight benzene derivatives with the following substituents: -O-CH_3, -N=O, -CH_2-CH_3, -CH=CH_2, -CH=O, -OH, -COOH, and -(CO)-CH_3 (the two last substituents represent a family of branched nonsymmetric groups). These calculations supplied, among others, the optimal values ψ_o and φ_o of the exocyclic angles ψ and φ for each compound. In addition to the unconstrained HF calculations, for each of these compounds two series of constrained geometry optimizations were performed at the HF/6-31G* level:

(i) by fixing the ψ angle at $\psi_o + \delta$, δ = 4, -4, -8, and -12°;

(ii) by fixing the φ angle at $\varphi_o + \delta$, δ = 2, -2, -4, and -6°.

The unconstrained geometry optimizations and the constrained optimizations (i) and (ii) produced altogether 9 sets of geometries for each of the 8 benzene derivatives considered. These sets of data were then subjected to correlation analysis. For studying the effect of bond alternation within the phenyl ring, two subsets of intra-ring C-C bonds, each corresponding to non-neighbouring bonds, were considered (see Fig. 3):

$$A = \{R_1, R_3, R_5\} \quad \text{and} \quad B = \{R_2, R_4, R_6\}$$

For any pair of bonds, we analysed the correlation between the corresponding sets of bond lengths. It was found that the correlation coefficients calculated for a pair of bonds which belong both either to A or B are always positive, whereas for a pair of bonds which belong to different subsets, i.e. one to A and the other to B,

the correlation coefficients turned out to be always negative. The signs of the correlation coefficients indicate that, as a result of a perturbation due to the bending of either ϕ or ψ angle, all the bonds belonging to A become elongated (or shortened), while those belonging to B become shortened (or elongated). The above finding provides statistical evidence for the AGIBA effect in mono-substituted benzenes.

Origin of the AGIBA effect in mono-substituted benzenes

For a more detailed analysis of the molecular-geometry changes caused by attaching an angular group to the benzene ring, we have chosen 10 substituents: -O-CH_3, -N=O, -CH_2-CH_3, -CH=CH_2, -NH-NH_2, -N=NH, -N=CH_2, -NH-CH_2, SH and -OH. For the corresponding phenyl derivatives, we have carried out HF/6-311G** calculations with full optimization of the molecular geometry. The results of these calculations are summarized in Table 1; for each compound the Kekule-structure ratio, the bond-length differences R_1 - R_6 and R_3 - R_4, the valence-angle differences φ - φ' and ω - ω', and the barrier to rotation (computed from separate HF/6-311G** optimizations with the XY groups constrained to be in the mirror plane) are given.

Table 1. HF/6-311G** data for mono-substituted benzenes.

No.	Angular group -X-Y	Kekule-structure weights† (%)	R_1- R_6 (Å)	R_3 -R_4 (Å)	φ - φ' (°)	ω - ω' (°)	Barrier to rotation (kJ/mole)
1.	-O-CH_3	59.4 : 40.6	-0.009	-0.013	8.9	1.9	6.1
2.	-N=O	44.0 : 56.0	0.008	0.008	7.8	-1.9	33.2
3.	-CH_2-CH_3	56.9 : 43.1	-0.008	-0.008	4.9	1.6	-5.1
4.	-CH=CH_2	45.2 : 54.8	0.005	0.007	4.5	1.2	11.7
5.	-NH-NH_2	57.2 : 42.8	-0.007	-0.010	3.1	0.9	38.8
6.	-N=NH	43.7 : 56.3	0.009	0.008	8.5	-1.6	20.4
7.	-O-H	53.9 : 46.1	-0.003	-0.006	5.0	-0.1	10.7
8	-SH	51.4 : 48.6	-0,002	-0.002	5.1	0.8	-2.6
9.	-NH-CH_3	55.9 : 44.1	-0.006	-0.008	2.2	1.0	29.9
10.	-N=CH_2	46.9 : 53.1	0.006	0.004	10.6	3.2	-1.3
11.	-H‡	52.4 : 47.6	-0.006	-0.001	8.4	2.6	—

†The first and the second Kekule structure correspond to the bond-alternation patterns of the phenyl ring shown in Figs. 2a and 2b, respectively.

‡Constrained optimization keeping the ϕ and ω angles equal to that of anisole (No. 1).

The entries 1-10 in Table 1 give rise to the following observations:

(i) The barriers to rotation are positive, indicating the stability of the planar forms of all the molecules except ethylbenzene, N-methylidenoaniline and thiophenol. The magnitude of a barrier reflects the interplay of a π-electron coupling between the substituent and the phenyl ring and steric factors. As seen, the size of the AGIBA effect is not correlated with the values (or even signs) of the barrier to rotation.

(ii) For each molecule, the bond-length differences R_1 - R_6 and R_3 - R_4 are of the same sign and very similar magnitude, indicative of the propagation of bond length alternation within the phenyl ring.

(iii) The bond-length differences R_1 - R_6 and R_3 - R_4 are negative for the molecules 1, 3, 5, 7, 8 and 9 and positive for the molecules 2, 4, 6 and 10. This is in agreement with the general rule stated in the Introduction.

(iv) For all the molecules 1-10, the valence-angle differences φ - φ' are positive and quite large, ranging from 2.2 to 10.6°;

(v) The valence-angle differences ω - ω' are usually also positive (with the exception of those for molecules 2, 6 and 7), but smaller than the differences φ - φ'.

It follows from observation (i) that there is a coupling between the π-electron sub-system of the phenyl ring and that of the -X-Y (or -X=Y) group, which favours the planar conformation of molecules 1-2 and 4-7. Within the conventional resonance-theory picture, this coupling should be of a through-bond type, i.e. is mediated through a partial π bond between atoms C_1 and X. Such a coupling should lead to a quinoid-type canonical structure and cannot account for the observed non-zero differences R_1 - R_6 and R_3 - R_4.

Observations (iv) and (v) indicate that the presence of an angular group introduces some strain in the part of the σ-electron skeleton involving fragments Y and X, and atoms C_1, C_2 and H_2, see Fig. 3. When both of the differences φ - φ' and ω - ω' are positive, one may interpret the strain as being the consequence of a repulsive interaction between H_2 and Y. However, in the case of the -N=O and -N=NH groups, the values of ω - ω' are negative, most likely because of an attractive interaction between the lone pair of the Y fragment with the H atom. Such an interaction cannot account for the large positive values of the corresponding diffrences φ - φ'. Therefore, it seems that, at least in these two cases, the strain at the C_1 atom is caused by a repulsive, through-space interaction between the π-electron subsystem of the phenyl ring and that of a -X=Y group. The case of phenol (entry No. 7), for which the difference ω - ω' is equal to -0.1°, is difficult to explain, because in this case the Y fragment is simply hydrogen, and therefore a through-space π-electron interaction is missing.

It should be noted that the benzene ring is susceptible to bond alternation ("bond fixation") under an influence of strain resulting from deformations of exocyclic valence angles. This was demonstrated by Stanger[6], who calculated the geometry of the benzene ring in which the pairs of neighbouring C-H bonds were bent in the molecular plane until they were pairwise parallel. The emerging pronounced bond fixation was a consequence of re-hybridization at each carbon centre: of two C-C σ-bonds attached to each centre, the one adjacent to the smaller exocyclic valence angle acquired an enhanced 2p-orbital character, whereas the one adjacent to the larger exocyclic angle acquired an enhanced 2s-orbital character. In the first case, the bond became weaker, and therefore longer; the opposite changes were in effect in the second case. This "re-hybridization effect" may contribute also to the AGIBA effect, through the distortion of the exocyclic valence angles at the C_1 atom [see observation (iv)] and the C_2 atom [see observation (v)]. To find out the magnitude of this kind of distortion alone, we carried out a HF/6-311G** constrained geometry optimization for benzene with the φ and ω angles equal to those in anisole (Table 1, entry No. 1); the results are presented in the entry 8 of Table 1. These results indicate the bond-alternation pattern expected for the "re-hybridization effect", with the differences R_1 - R_6 and R_3 - R_4 both being negative, in qualititative agreement with the bond-alternation pattern characteristic for a -X-Y

group, see Fig. 2a. However, the magnitudes of the bond-length differences are in this case smaller than for anisole, which indicates that the "re-hybridization effect" alone cannot fully account for the AGIBA effect for a -X-Y group. Let us note that in the case of a -X=Y group the bond-alternation pattern of Fig. 2b requires the "re-hybridization" effect to be overcome by the postulated through-space π-electron interaction between the substituent group and the phenyl ring.

Following the idea set forth in Ref. 22, we have carried out additional HF/6-31G* (constrained) geometry optimizations for mono-substituted benzenes by keeping the C_1-X-Y plane perpendicular to the phenyl-ring plane, and fixing the φ angle at φ_o (the optimal value resulting from the planar molecule optimization using the same basis set). The (R_1-R_6) differences for the planar (unconstrained) and perpendicular (constrained) molecular structures are shown in Diagram 1.

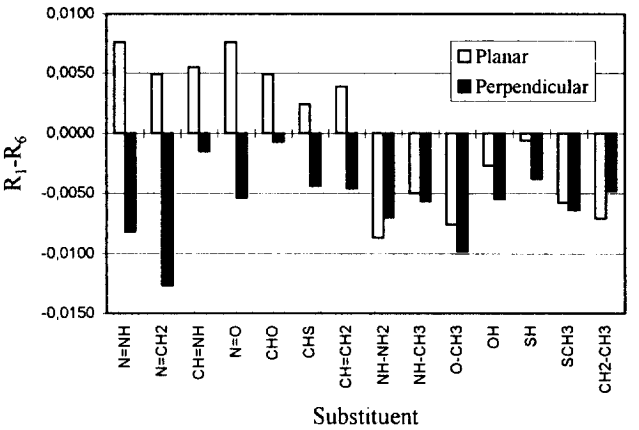


Diagram 1. Bond-length differences (R_1-R_6) in Å corresponding to HF/6-31G* optimized structures: planar (unconstrained optimization) and perpendicular (constrained optimization, see text).

As argued in Ref. 22, by making the C_1-X-Y plane perpendicular to the ring plane, this effectively switches-off the through-space π-electron interactions of the angular group with the ring. On the other hand, by keeping the φ_o angle fixed at the optimal value for the planar molecule, this leaves the strain at the C_1 atom almost unchanged. As a result, the purely "re-hybridization" component of the AGIBA effect should show up in this case. The results shown in Diagram 1 indicate that this is indeed the case. Both, the overall AGIBA effect and its "re-hybridization" component depend markedly on the substituent. The overall AGIBA effect for X=Y groups is directed oppositely to its "re-hybridization" component. Therefore the through space π–electron interaction is the dominant one, outweighing the "rehybridization" effect. In the case of X-Y groups, the "rehybridization" seem to be the dominant component of the AGIBA effect.

Conformation dependence of the effect

It has been shown for 1,4-homo-disubstituted benzene derivatives that the AGIBA effect depends on the conformation[20, 23]. It results in an enhancement of the effect for the *cis* derivatives and in a very small effect for

the *trans* ones. This effect is also expected in 1,3-homo-disubstituted derivatives of benzene. Fig. 4 presents optimized geometry of 1,3-dinitroso and 1,3-dimethoxy derivatives of benzene, calculated with RHF/6-311G** level for two different conformations: symmetrical (4a, 4c) and non-symmetrical (4b, 4d). For each molecule, only one of possible two symmetrical conformers is considered since the results for the other one are qualitatively similar. In the case of the symmetrical conformations (4a, 4c) the AGIBA effect is small, due to symmetry with no imbalance of the Kekule structures weights. In non-symmetrical conformations (4b, 4d) the effect is enhanced by factor 2/3 and the imbalance of the Kekule structure weights is substantial: 66 : 34 for 1,3-dimethoxy derivative and 38 : 62 for 1,3-dinitroso derivative. This is an additional proof for the rule depicted in Fig. 2 and suggests additivity of the effect.

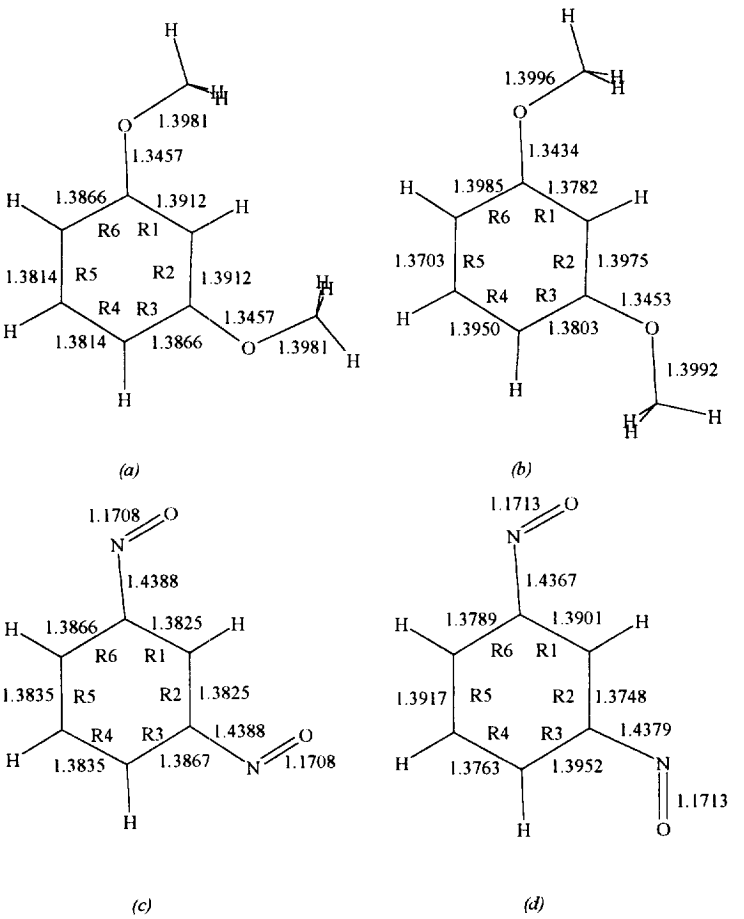


Figure 4. Bond lengths for different conformations of: *(a)* and *(b)* - 1,3-dimethoxybenzene, *(c)* and *(d)* - 1,3-dinitrosobenzene.

Since the barriers to rotation for the substituents are up to 38.8 kJ mole^{-1} (Table 1), it may be concluded that temperature-dependent measurements of certain spectral properties could provide an appropriate way of experimentally investigating AGIBA.

Conclusions

In conclusion, it may be stated that angular substituents in benzene derivatives induce bond alternation in the ring. It seems that the AGIBA effect is a net result of two competing mechanisms. The first is due to through-space π electron interactions between the group and the ring, and the second corresponds to a rehybridization effect which is due to the angular strain at the ipso carbon atom. The magnitude of AGIBA in monosubstituted benzene derivatives is around 0.01Å. The effect is small but statistically significant. It is structurally well observed and may be a reason of physicochemical consequences in molecules of the appropriate - and frozen - conformations.

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