Pergamon

Tetrahedron 54 (1998) 3533–3548

TETRAHEDRON

Angular Group-Induced Bond Alternation
II. The Magnitude and the Nature of the Effect and its Application to Polynuclear Benzenoid Systems*

Sian T. Howard,[a] Tadeusz. M. Krygowski,[b] Aarkadiusz. Ciesielski,[c] Marcin. Wisiorowski[b]

[a] Department of Chemistry, University of Wales, Cardiff, Cardiff CF1 3TB, U. K.
[b] Department of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warsaw, Poland.
[c] Institute of Biochemistry and Biophysics Polish Academy of Sciences, ul. Pawińskiego 5a, 02 106 Warsaw, Poland

Received 13 October 1997; accepted 29 January 1998

Abstract By careful selection of `angular' substituents it is possible to induce sizeable deformations of benzene ring structures, which correspond to bond length alternation. *Ab initio* calculations are used to explore the range of this effect in 1,3,5-trisubstituted benzenes with 14 different substituents (-CH_2NH_2, -OCH_3, -CH_2CH_3, -SCH3, -$NHNH_2$, -$NHCH_3$, -OH, -SH, -N=CH_2, -CH=CH_2, -COH, -N=O, -N=NH, -CH=NH). The effect is strongly conformation-dependent, and for C_3-symmetrical compounds is additive, in the sense that the induced π-localization is three times larger than in the analogous mono-substituted benzenes. This reflects a new approach to understanding how substituent effects operate in organic chemistry, which is not directly related to `electron-withdrawing' or `electron-donating' power, but rather on the substituent conformation (and on whether it contains single or double bonds). The effect is explored in polynuclear benzenoid systems (the trimethoxyphenalene cation, and tetramethoxyperylene). The nature of the effect is examined by analyzing the ring and substituent energies. Finally, the probable chemical consequences of such substitution pattern are discussed.

Introduction

It has long been known that the benzene ring may be seriously deformed when it is fused to one or several rings.[1-8] Changes of bond lengths in naphthalene (**1**), phenanthrene (**2**) and triphenylene (**3**) illustrate well the effect for aromatics. In the case of small rings fused to benzene, the effect is even stronger as shown by compounds (**4**)-(**9**) presented in Figure 1. However, it should be taken into account that bonds in such rings are in fact bent (`banana bonds') and typically have bond path lengths differing from the internuclear distance[9] (which influences how we measure the geometry).

---

* Dedicated to Professor Günter Häfelinger (Tübingen) on the occasion of His 60th birthday

PII: S0040-4020(98)00087-8

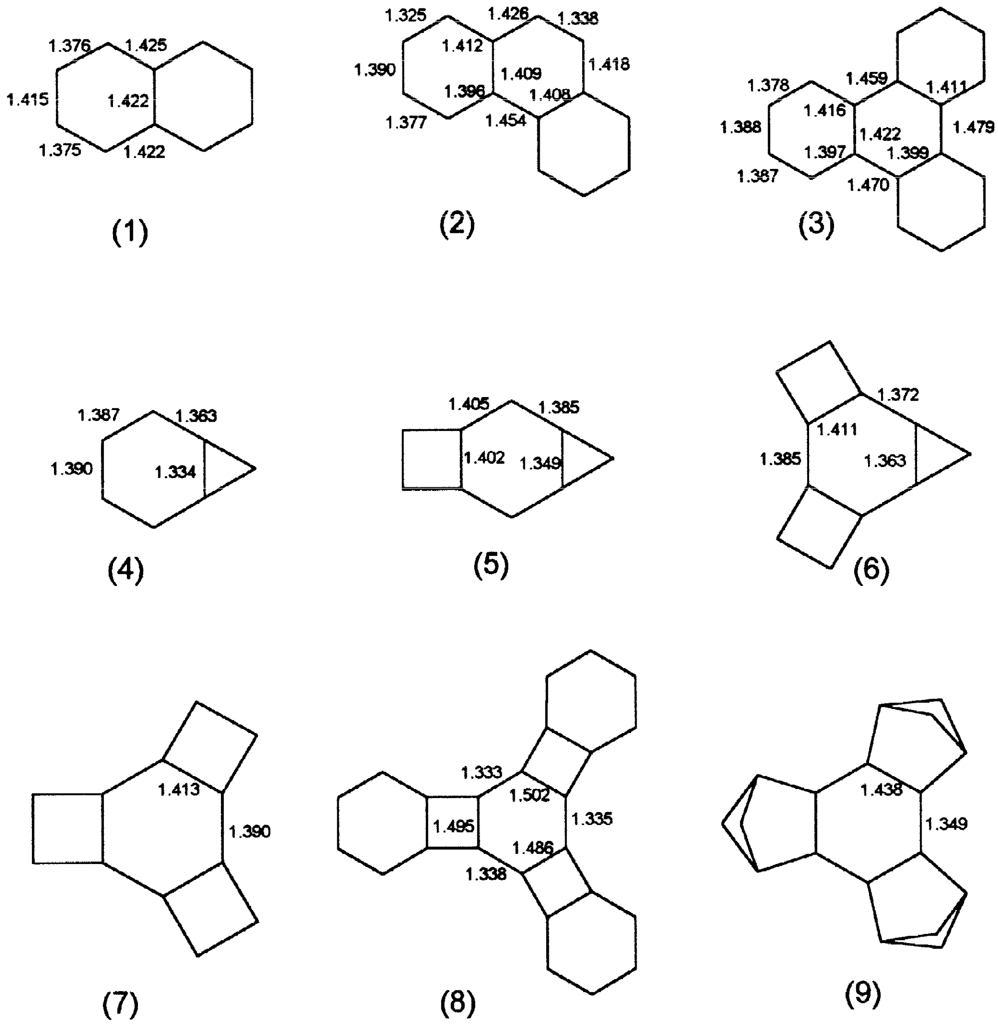


Fig 1. Experimental geometries of (1) naphthalene,[10] (2) phenanthrene,[11] (3) triphenylene,[12] (4) 1H-cyclopropabenzene,[13] (5) 3,4-dihydro-1H-cyclobuta[a] cyclopropa[d]benzene,[14] (6) 1,3,4,5-tetrahydrodicyclobuta[a,c]cyclopropa[e]benzene,[15] (7) 1,2,3,4,5,6-hexahydrotricyclobuta [a,c,e]benzene,[15] (8) tris(benzocyclobutadieno)benzene,[16] (9) trisbicyclo[2.1.1]hexanobenzene.[17]

These deformations associated with fused rings have often been interpreted in terms of the 'Mills-Nixon' effect.[18] Undoubtedly any kind of ring fused to benzene leads to deformation of the regular hexagon, causing localization of the π-electron structure which is strongly dependent on the nature of the fused ring(s) (see the examples in Figure 1). The observed pattern of deformation in compounds (4)-(9) is typically an alternation of bond lengths, which could be seen as the preferential selection of one Kekule structure over the other.

Acyclic substituents attached to benzene rings will also cause some deformation of the ring, although this does not usually result in the bond length alternation mentioned in the previous paragraph. However, it has been recently shown[19-24] that 'angular' substituent groups can cause the same pattern of bond length alternation found in the cases of fused rings — see Figure 2.

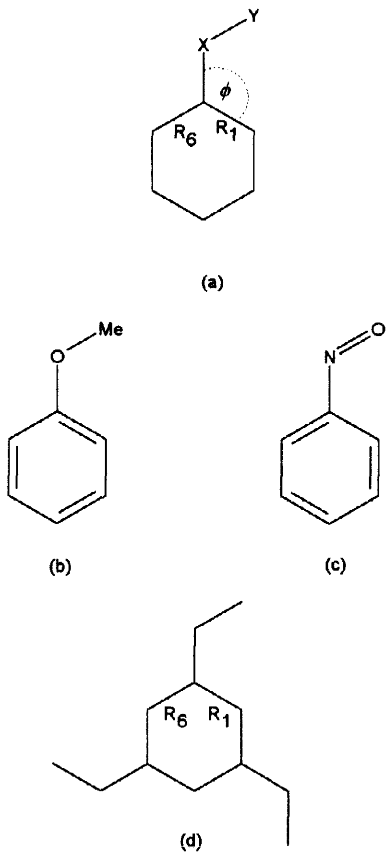


Fig. 2. (a) Schematic diagram of a monosubstitued benzene with an angular substituent -XY; (b) Operation of AGIBA with single-bonded substituents; (c) Operation of AGIBA with double-bonded substituents; (d) Definition of bond labels in 1,3,5-trisubstituted benzenes with angular substituents

We have termed the effect 'Angular Group-Induced Bond Alternation' (AGIBA).[23] A remarkable feature of this effect is that substituents containing single bonds induce the opposite Kekule structure to those with double-bonded substituents. To make this clearer: the methoxy substituent shortens the ring bond (R1) which is *cis* to it, lengthens the ring bond (R6) which is *trans* to it, and the alternation is propagated around the ring (see Figure 2). The nitroso group lengthens R1, shortens R6, and also propagates bond length alternation.

In the most recent work, we attempted to identify the basis of this effect in monosubstituted benzenes.[23] In such compounds the effect is rather weak (bond lengths alternate by ≈ 0.01Å at most. We considered three possible mechanisms which may contribute to AGIBA:

(i) σ or π conjugation (depending on the class of substituent),

(ii) re-hybridization of the α-carbon atom,

(iii) a through-space interaction with the ring.

In general, all three effects can certainly affect the ring geometry. In the case of (i), this clearly has a symmetrical effect on the ring geometry, so it does not contribute to AGIBA. The re-hybridization effect (ii) is due to an opening of the angle ϕ (see Figure 2), which acts to shorten the *cis* bond for *all* angular substituents.

The last effect (iii) seems to be the dominant one. It acts in concert with effect (ii) in the case of single-bonded substituents, and oppositely for double-bonded substituents.

In this paper, we explore AGIBA in classes of compounds where the induced bond length-alternation is sufficiently large[20-22] that the ring must become markedly less aromatic, leading (we suggest) to observable chemical consequences. In planar 1,3,5-trisubstituted benzenes (C_{3h} symmetry), only two unique bond lengths are present in the ring (unlike in mono-substituted or di-substitued species). We therefore consider these compounds to be the most convenient and convincing models for characterizing AGIBA for a particular substituent. We will classify the magnitude of the effect according to the types of substituents, and investigate the additivity with respect to the number and nature of substituents. This is followed by a short analysis of AGIBA in terms of ring-substituent interaction energies, using the energy decomposition scheme of Bader[9]. Examples of AGIBA in fully-substituted benzenes and polycyclic benzenoid systems are then presented. Finally, the possible chemical consequences and applications of AGIBA are discussed.

Computational Details

The Hartree-Fock calculations were carried out with GAMESS[25] running on DEC Alpha RISC workstations, and GAUSSIAN94[26] running on a Cray YMP-932 at Rutherford Appleton Laboratories, Oxfordshire. The topological analysis of ρ utilized the program SADDLE[27]. The 6-311G** basis set[28] was used for the 1,3,5-trisubstituted benzenes, which were all optimized in C_{3h} symmetry. The slightly smaller 6-31G** basis set[29] was used for the polycyclic benzenoid species, which were optimized in the following symmetries: D_{2h}, C_{2v} (naphthalene and tetramethoxynaphthalene); C_{3v}, C_3 ([phenalene]$^+$ and [trimethoxyphenalene]$^+$); and D_{2h}, C_2 (perylene and tetramethoxyperylene). BLYP/6-311G** geometry optimizations of 1,4-disubstituted species were also carried out on the Cray YMP 4E and SGI ONYX at Warsaw University's Interdisciplinary Centre for Mathematical and Computational Modeling. The total energy decomposition scheme of Bader has been applied to determine the separate energies of the rings and substituents in these compounds, using the AIMPAC programs.[27]

Results and Discussion

1,3,5-trisubstituted benzenes

Table 1 presents the results of fourteen HF/6-311G** optimizations on the 1,3,5-trisubstituted benzenes with various substituents. The size of AGIBA is measured by the difference between adjacent ring bond lengths R1-R6, and is compared with the same quantity in monosubstituted benzenes computed at the same level of theory (results taken mostly from[23]). The largest effects are observed for the single-bonded substituents -CH_2NH_2, -OCH_3 and -CH_2CH_3, whilst the largest double-bonded effects are found for the groups -CH=NH, -N=O and -

N=NH. It is observed that, in line with what was observed for 10 monosubstituted benzenes[23], single-bonded substituents cause shortening of R1 and lengthening of R6, whilst double-bonded substituents have the opposite effect. The slightly stronger observed effect for single-bonded substituents is a consequence of the fact that AGIBA is a sum of two effects which act in the same direction (through-space and re-hybridization), whereas they oppose each other in doubly-bonded substituents. The size of the effect in these largest cases (≈ 0.03Å) is highly significant, as verified by experimental structural studies,[20-22] and should be expected to have chemical consequences.

Table 1 Ring Bond Lengths (Å) In 1,3,5-trisubstituted Benzenes (HF/6-311G** level)

Group	R1, R6*	R1-R6 (trisubstituted)	R1-R6 (monosubstituted)	[R1+R6]/2
-H**	1.3855, 1.3855	0.0	0.0	1.3855
$-CH_2NH_2$	1.3712, 1.4040	-0.033	-0.010	1.3876
$-OCH_3$	1.3740, 1.4021	-0.028	-0.009	1.3881
$-CH_2CH_3$	1.3750, 1.4025	-0.028	-0.008	1.3888
$-SCH_3$	1.3758, 1.3998	-0.024	-0.007	1.3878
$-NHNH_2$	1.3835, 1.4065	-0.023	-0.007	1.3950
$-NHCH_3$	1.3855, 1.4061	-0.021	-0.006	1.3958
-OH	1.3812, 1.3903	-0.009	-0.003	1.3858
-SH	1.3833, 1.3890	-0.006	-0.002	1.3862
$-N=CH_2$	1.3934, 1.3812	0.012	0.006	1.3873
$-CH=CH_2$	1.3981, 1.3811	0.017	0.005	1.3896
-COH	1.3975, 1.3773	0.020	0.005	1.3874
-N=O	1.3958, 1.3731	0.023	0.008	1.3845
-N=NH	1.3966, 1.3735	0.023	0.009	1.3851
-CH=NH	1.3997, 1.3761	0.024	0.007	1.3879

*) The bonds R1 and R6 are defined in Figure 2.

**) The values for unsubstituted benzene.

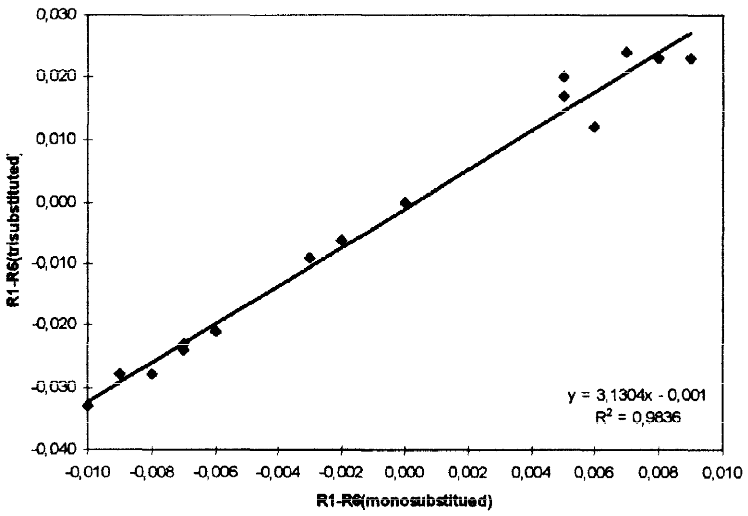


Fig. 3 The relationship between the size of AGIBA in fourteen monosubstituted and 1,3,5-trisubstituted benzenes and the unsubstituted benzene (HF/6-311G** level). The correlation coefficient is +0.992, and the gradient of the trend-line is 0.314.

Figure 3 shows the relationship between these two sets of data. The excellent linear correlation (r=0.984) and slope of 0.313 demonstrates that the AGIBA effect is almost exactly additive with respect to the number of substituents. The larger scatter of points on the right-hand side of Figure 3, which correspond to doubly-bonded substituents, may also reflect the fact that AGIBA is a sum of two effects acting oppositely in these cases, which worsens the correlation. It is also an interesting observation that the *mean* ring bond length (R1+R6)/2 is larger than that of benzene (1.3855Å at the HF/6-311G** level) in 11 of the 14 cases, with a highest mean value of 1.396Å. This indicates that AGIBA is accompanied by a general slight expansion of the ring, although there is no correlation between (R1+R6)/2 and the size of AGIBA.

Although strong bond length alternation demonstrably exists in many of these 1,3,5-trisubstituted benzenes, it is important to show the connection between these geometry changes and changes in the π-electron structure. A very convenient measure of the latter is the so-called bond ellipticity[30] ε, which is based directly on the electron density ρ in the bond. It measures the asymmetry between the principal curvatures of ρ pointing perpendicular to the bond (λ_1, λ_2) at the 'bond critical point' (where $\nabla\rho = 0$): $\varepsilon=\lambda_2/\lambda_1-1$. A pure single bond is cylindrically symmetrical ($\varepsilon=0$). The double bond of ethene has $\varepsilon \approx 0.4$, and intermediate character bonds such as in benzene derivatives typically have $\varepsilon \approx 0.2$-0.3.

Table 2. Ring Bond Ellipticities In 1,3,5-trisubstituted Benzenes (HF/6-311G** level)}

Group	ε(R1)	ε(R6)	[ε(R1)+ε(R6)]/2	ε(R1)-ε(R6)
-H*	0.232	0.232	0.232	0.0
-CH_2NH_2	0.284	0.210	0.247	0.074
-OCH_3	0.355	0.271	0.313	0.084
-CH_2CH_3	0.275	0.210	0.243	0.065
-SCH_3	0.286	0.228	0.257	0.058
-$NHNH_2$	0.346	0.277	0.312	0.069
-$NHCH_3$	0.341	0.281	0.311	0.060
-OH	0.338	0.305	0.322	0.033
-SH	0.271	0.256	0.264	0.015
-N=CH_2	0.241	0.279	0.260	-0.038
-CH=CH_2	0.209	0.258	0.234	-0.049
-COH	0.188	0.237	0.213	-0.049
-N=O	0.201	0.262	0.232	-0.061
-N=NH	0.213	0.277	0.245	-0.064
-CH=NH	0.192	0.252	0.222	-0.060

$^{*)}$ The values for unsubstituted benzene

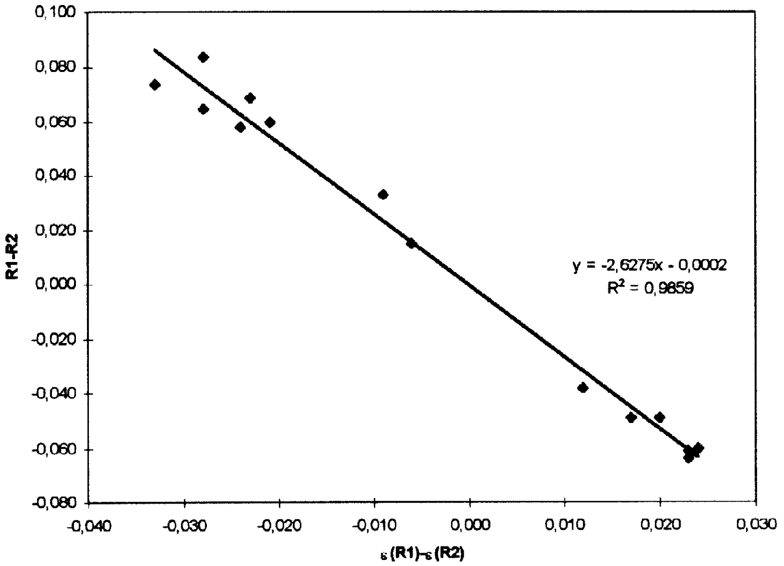


Fig. 4. The relationship between the differences in ellipticity between adjacent ring bonds and the size of AGIBA (measured by R1-R6) in fourteen 1,3,5-trisubstituted benzenes and unsubstituted benzene (HF/6-311G** level). The correlation coefficient is -0.992.

Table 2 presents ring bond ε values for the 1,3,5-trisubstituted benzenes, together with the mean ring bond ellipticities and the differences between ellipticities of the adjacent ring bonds. The ε values often differ greatly from the parent compounds benzene (39% larger in the most extreme case), so there is no doubt that 1,3,5-substitution causes large, measurable changes in the π-electron structure.

Figure 4 shows the relationship between the size of AGIBA and the differences in adjacent bond ellipticities. Clearly there is an excellent correlation, which demonstrates that the bond length alternation is directly linked to changes in the distribution of π electrons. There is no correlation between the mean values of ε and the size of AGIBA. However, an interesting observation is that the mean ring bond ellipticity is increased relative to benzene for *all* single-bonded substituents, whereas there is little change relative to benzene for the double-bonded substituents. We currently have no explanation for this, but there is further evidence that these two classes of substituents act in fundamentally different ways.

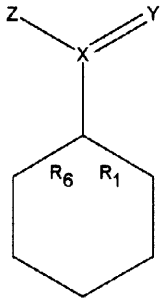


Fig. 5. Schematic diagram illustrating the labelling of bonds and atoms in 'branched' substituents.

We also briefly consider the case of 'branched' substituents, where the atom X is doubly-bonded to Y and singly-bonded to Z (Figure 5), where Z is a non-hydrogen atom. We take the examples of the carboxy and acetyl groups CO_2H and $COCH_3$. It could be anticipated that such groups might give rise to a large AGIBA effect, since the sub-group X=Y could induce a *trans* double-bond in the ring, and the sub-group X-Z should induce double-bond character in the ring bond *cis* to it, thus both acting in the same direction. Large AGIBA's could result, especially in 1,3,5-trisubstituted compounds with such branched substituents. However, the HF/6-311G** optimized R1-R6 values for 1,3,5-tricarboxybenzene (0.006Å) and 1,3,5-triacetylbenzene (0.017Å) show that the situation is more complex. In the first case, the AGIBA effect is very small, much smaller than it is found in 1,3,5-triformylbenzene (0.020Å) in which Z is a hydrogen atom. In the second case the effect is larger, but still much smaller than the sum of the effects for the angular groups in 1,3,5-triformylbenzene and 1,3,5-triethylbenzene (0.020+0.028=0.048Å). Since this paper concentrates on the range and nature of the AGIBA effect, we defer an analysis of this more complicated case to another work.

Energetics of AGIBA

The bond alternation described in the previous section could be associated with the interaction energy between the substituent and the ring. One of the simplest ways to estimate this interaction is the barrier to rotation of the substituent; but in Paper I[23] it was established that there is no link between this quantity and the size of AGIBA. Here we follow an approach to quantifying these interactions, using the total energy decomposition scheme of Bader[9] to determine separately the energies of substituents and rings. This is carried out by evaluating the energies of each atom in the system, and then summing to give a ring subsystem energy and a substituent subsystem energy (in fact, the latter is just the total energy of the system minus the ring energy).

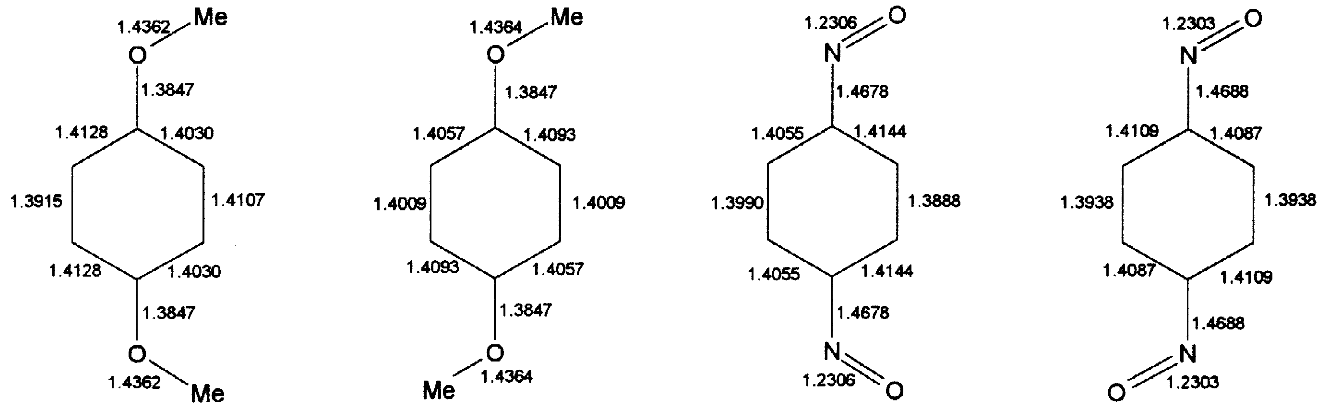


Fig. 6 Structures of *cis* and *trans* conformers of 1,4-dimethoxybenzene and 1,4-dinitrosobenzene, calculated at the BLYP/6-311G** level.

Figure 6 illustrates the BLYP/6-311G** optimized structures of *cis* and *trans* conformers of 1,4-dimethoxybenzene and 1,4-dinitrosobenzene. In both cases, the *cis* conformers show a marked AGIBA effect, whereas the *trans* conformers show essentially no alternation. The total energy difference E(*cis*)-E(*trans*) is chemically insignificant, as could be expected: -0.7 kJ·mol^{-1} in dimethoxybenzene and -0.6 kJ·mol^{-1} for dinitrosobenzene.

Table 3. Energies for 1,4-dinitrosobenzene isomers.

Compound	Total energy (E_{TOTAL}) obtained at BLYP/6-311G** level	Extracted energy of benzene ring (E_{RING})
cis-1,4-dinitrosobenzene	-490,84308259 [Ha]	-230,61719742 [Ha]
trans-1,4-dinitrosobenzene	-490,842837619 [Ha]	-230,6184084 [Ha]
Differences in energy	$E^{cis}_{TOTAL} - E^{trans}_{TOTAL}$ = -0.64 kJ/mol	$E^{cis}_{RING} - E^{trans}_{RING}$=3.18 kJ/mol

Table 4. Energies for 1,4-dimetoxybenzene isomers.

Compound	Total energy (E_{TOTAL}) obtained at BLYP/6-311G** level	Extracted energy of benzene ring (E_{RING})
cis-1,4-dimetoxybenzene	-461,24012105 [Ha]	-230,3576955 [Ha]
trans-1,4-dimetoxybenzene	-461,23985372 [Ha]	-230,3580303 [Ha]
Differences in energy	$E^{cis}_{TOTAL} - E^{trans}_{TOTAL}$ = -0,70 kJ/mol	$E^{cis}_{RING} - E^{trans}_{RING}$ = 0,88 kJ/mol

Tables 3 and 4 present the energetic decomposition described above for these two systems. The results suggest that the ring is slightly less stable in the *cis* conformers (although again the energy differences are very small, 0.88 kJ·mol^{-1} and 3.18 kJ·mol^{-1} respectively). This is consistent with the idea that the rings should be less aromatic (and therefore less stable) because of π-electron localization. Using the changes in total and ring subsystem energies between *cis* and *trans* conformers, we can deduce that the substituents are slightly stabilized in the *cis* conformers, *i.e.* AGIBA is accompanied by a transfer of energy from the ring to the substituent. However, these energy changes are very small: the substituent energies are more stable by 1.6 kJ·mol^{-1} and 3.8 kJ·mol^{-1} in dimethoxybenzene and dinitrosobenzene, respectively.

Fully-substituted benzenes

Since we have shown that substituents such as methoxy and nitroso induce opposite patterns of bond length alternation, a fully-substituted benzene such as 1,3,5-trimethoxy-2,4,6-trinitrosobenzene logically could show a very enhanced AGIBA effect. Figure 7a shows the HF/6-311G** optimized structure of this compound C_{3h} symmetry has been assumed), and AGIBA is indeed very large (R1-R6=0.044Å). A remarkable feature of this structure is the near-linear nitroso groups. This suggests that the nitroso groups in this structure do not contribute to AGIBA in the usual way, since they are not `angular' and the through-space interactions have been lost. The opening of the O-C1-C2 and N-C2-C1 angles (130.9° and 124.4°) compared to the values in 1,3,5-trimethoxybenzene (124.1°) and 1,3,5-trinitrosobenzene (123.1°) suggests that increased re-hybridization due to steric interactions between the groups is the basis for the increased AGIBA effect. But there is an alternative hypothesis, which is that nitroso is simply acting as an electron-withdrawing substituent, and this additional electronic effect is capable of enhancing AGIBA.

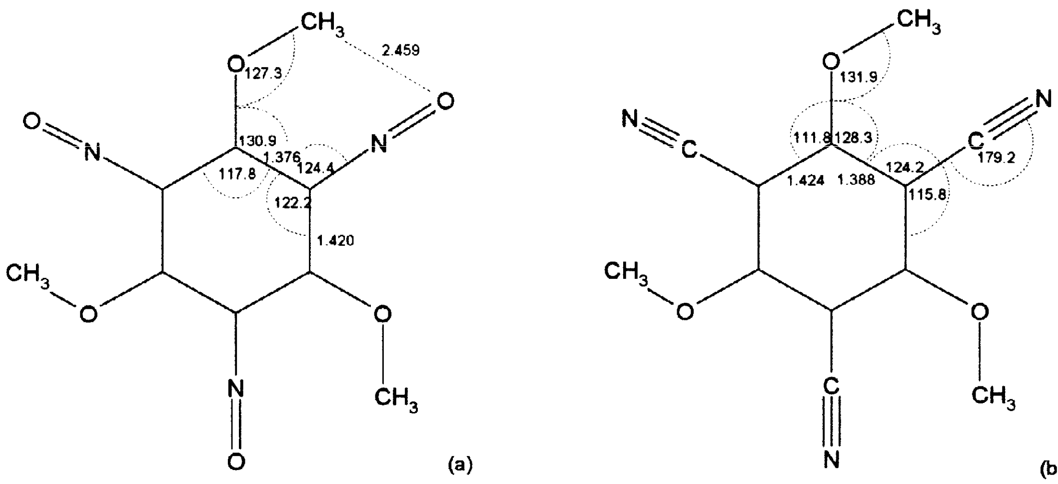


Fig. 7 Structure of (a) 1,3,5-trimethoxy-2,4,6-trinitrosobenzene, (b) 1,3,5-trimethoxy-2,4,6-tricyanobenzene optimized at the HF/6-311G** level and assuming C_{3h} symmetry.

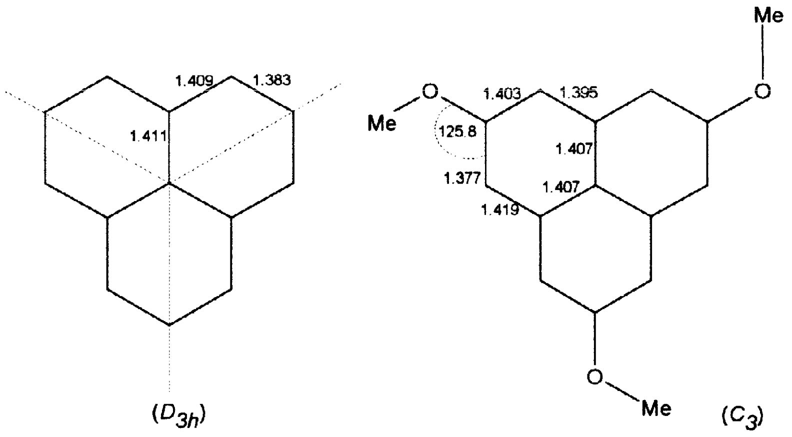
To explore this second possibility, we have optimized 1,3,5-trimethoxy-2,4,6-tricyanobenzene at the same level of theory (see Figure 7b), to see if this combination of substituents can also produce large AGIBA (the cyano group is a strictly linear, electron-withdrawing substituent). The changes in geometry are similar to those found for the previous case: the opening of the O-C1-C2 and C1-C2-C(N) angles (128.3° and 124.2°) suggest the same source of the enhancement of AGIBA, namely the re-hybridization effect.

AGIBA in polycyclic benzenoid compounds

In this final section, we intend to show how AGIBA operates in larger π- electron systems in which partial bond length alternation is already present in the unsubstituted hydrocarbons. In such systems, the definition of AGIBA is somewhat more problematic than in simple substituted benzenes or other species with all bond lengths equal (*s*-triazine, borazine). We therefore use the model 'HOSE' (Harmonic Oscillator Stabilization Energy),[31] which enables the estimation of the weights of the canonical (Kekule) structures using only the ring bond lengths .

We have selected a few polycyclic hydrocarbons with relatively high symmetry, in which several pairs of bonds have equal lengths. The methoxy group is used as the angular substituent, since this induces one of the largest effects. In each case, the conformations of the methoxy groups have been chosen to maximize AGIBA.

The Phenalene Cation



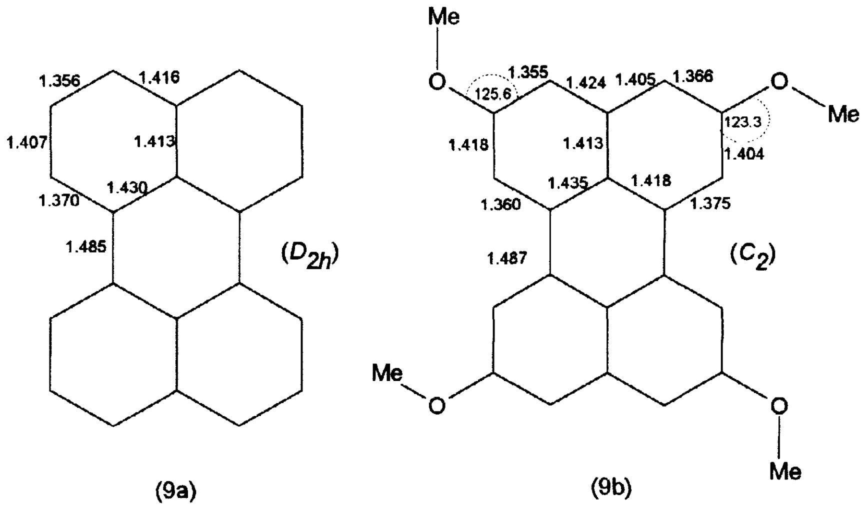
(8a) (8b)

Fig. 8. Structures of (a) the phenalene cation (b) [2,6,10-trimethoxyphenalene]$^+$ optimized with three-fold axis of symmetry, HF/6-31G** level.

The phenalene cation has D_{3h} symmetry, which is lowered to C_3 on substitution of methoxy groups in the 2-, 5- and 8- positions in a planar conformation as shown in Figure 8. The difference induced between the ring bonds *cis* and *trans* to the methoxy substituent is 0.026Å, which is comparable in size to the effect found in 1,3,5-trimethoxybenzene. Using HOSE to measure the imbalance in Kekule structures shows that the methoxy substituent causes an imbalance 63.8%:36.2%, indicating a substantial localization effect over that observed in the parent compound (50.0%:50.0%).

Perylene

Perylene has D_{2h} symmetry, which is lowered to C_2 by substitution at the 2-, 5-, 8- and 11- positions with the methoxy groups oriented as shown in Figure 9. In the parent compound, the alternation observed at the sites where methoxy will be substituted is already substantial (0.058Å). After substitution at these positions (symmetrically equivalent in perylene), the *cis—trans* bond length difference is slightly enhanced compared to perylene at one site (0.063Å), and decreased at the other site (0.038Å). This arises because the methoxy group is *cis* to a shorter bond in one case, and *cis* to a longer bond in the other. The fact that the induced bond length differences (*i.e.* compared to the value in perylene) are not so large may be due to some kind of saturation effect. In other words, it is difficult to substantially change the alternation between a pair of bonds which already show such a large difference in the parent compound. A more interesting observation is that a significant difference of 0.019Å is induced between the two central bonds between substituents (equal at 1.416Å in perylene), despite the fact that these bonds are well-removed from the substituents.



(9a) (9b)

Fig. 9. Structures of (a) perylene (b) 2,7,11,16-tetramethoxyperylene optimized with two-fold axis of symmetry, HF/6-31G** level.

The effect is more strongly illustrated by the HOSE-calculated weights of the two Kekule structures. In the parent compound, the imbalance for the outer rings is 22.9%:77.1%. As a result of methoxy substitution on the upper left-hand ring in Figure 9, where the methoxy group is *cis* to a shorter bond, the imbalance is increased over perylene (16.2%:83.8%). If the methoxy group is *cis* to a longer bond, as on the upper-right hand ring, the AGIBA effect acts to shorten this bond and to lengthen the bond *trans* to methoxy, leading to less Kekule imbalance (30.6%:69.4%).

Conclusions

Angular Group-Induced Bond Alternation (AGIBA) is found to operate quite strongly in a range of 1,3,5-trisubstituted benzenes (alternation of up to ≈ 0.03Å), the exact degree of π-localization being strongly dependent on the substituent. The effect is much weaker in mono- and symmetrically di-substituted benzenes, which is probably why the energetic analysis presented shows such small changes between different conformers. Unlike the di-substituted case, there is unfortunately no natural reference conformation which could be analysed as the *non AGIBA* case in 1,3,5-trisubstituted benzenes.

In fully-substituted benzenes and also in substituted polycyclic compounds, we can draw a distinction between two patterns of substitution:

(i) substituents are far-removed from one another (as in the phenalene cation and perylene examples,

(ii) substituents are sufficiently close to one another so that steric interactions between them contribute to AGIBA, probably by enhancing the contribution of re-hybridization. Examples of this include 1,3,5-trimethoxy-2,4,6-trinitrosobenzene, 1,3,5-trimetoxy-2,4,6-tricyanobenzene and tetramethoxynaphthalene.

In polynuclear aromatic compounds, the AGIBA effect is also shown to operate quite strongly, but in a more subtle way than in substituted benzenes. The strong local changes in bond length observed in the ring at the site of substitution in benzenes are generally not so evident in the polynuclear compounds, but there is a long-range response of bonds far-removed from the site of substitution.

It is hard to imagine that the sometimes substantial changes in π-electron localization presented here would not lead to significant changes in chemical properties of these compounds. Examples of applications of AGIBA might include:

(i) AGIBA may provide a synthetic means for tailoring the interactions between benzene rings and metallic centres in facially-bonded complexes, *e.g.* metallocenes.

(ii) AGIBA could be used to modify the charge transfer properties of aromatic compounds (most charge transfer salts contain aromatic groups).

(iii) AGIBA may be used to modify the conductivity or magnetic susceptibility in the types of aromatic compounds used in *e.g.* organic conducting polymers.

Perhaps the most general point is that AGIBA may be seen as a new type of substituent effect in organic chemistry, which unlike conventional ideas of 'electron-withdrawing', 'electron-donating' or 'through-conjugating' substituents emphasizes the importance of conformational selectivity in aromatizing/de-aromatizing a π-electron system. Changes in patterns of single bond/double bond localization in a ring must affect the pattern of reactivity. Further work is in progress using *ab initio* calculations, statistical analysis of crystal structures, and low-temperature NMR techniques, to try and identify some of these effects.

Acknowledgements

STH acknowledges the U.K. Engineering and Physical Sciences Research Council (EPSRC) for an Advanced Fellowship. Financial support for TMK by BST-502/24/97 is kindly acknowledged. MW acknowledges the Interdisciplinary Centre for Mathematical and Computational Modelling (Warsaw University) for computational facilities.

References:

1. a). Apeloig, Y.; Arad, D., *J. Am. Chem. Soc.* **1986,** *108*, 3241. b). Apeloig, Y.; Arad, D.; Halton, B. and Randall, C., *J. Am. Chem. Soc.* **1986,** *108*, 4932. c). Apeloig,Y.; Karni, M. and Arad, D., in *Strain and Its Implications In Organic Chemistry*, De Meijere, A. and Blechert, S., Eds.; Kluwer Academic Publishers, Dodrecht, The Netherlands **1989**, 457.

2. Mo, O.; Yanez, N.; Eckert-Maksic, M. and Maksic, Z. B., *J. Org. Chem* **1995,** *60,* 1638 and references therein.

3. a). Eckert-Maksic, M.; Hodoscek, M.; Kovacek D.; Mitic, D.; Maksic, Z. B. and Poljanec, K., *J. Mol. Struct. THEOCHEM* **1990,** *65,* 89. b). Maksic, Z. B.; Eckert-Maksic, M.; Kovacek, D and Margetic, D., *J. Mol. Struct. THEOCHEM* **1992,** *92,* 89. c) Eckert-Maksic, M.; Maksic, Z. B. Hodoscek, M. and Poljanec, K., *Int. J. Quant. Chem.* **1992,** *42,* 869.

4. Hiberty, P.C.; Ohanessian, G. and Delbecq, F., *J. Am. Chem. Soc.* **1985,** *107,* 3095.

5. a) Halton, B. *The Chemistry of the Cyclopropenyl Group,* Vol. 2, Ch. 12, Rappaport, Z. Ed., J. Wiley **1995**, 707 ff. b) Halton, B., *Chem. Rev.* **1989,** *89,* 1161.

6. Stanger, A. , *J. Am. Chem. Soc.* **1991,** *113,* 8277.

7. Faust, R.; Glendening, E. D.; Streitweiser, A. and Vollhardt, K.P.C., *J. Am. Chem. Soc.* **1992,** *114,* 8263.

8. Eckert-Maksic, M.; Hodoscek, M.; Kovacek, D.; Maksic, Z. B. and Poljanec, K., *Chem. Phys. Lett.* **1990,** *171,* 49.

9. Bader, R.F.W., *Atoms In Molecules; A Quantum Theory,* Oxford University Press **1990**, Oxford.

10. Brock, C. P. and Dunitz, J. D., *Acta Cryst* **1982,** *38 B,* 2218.

11. Patricek, V.; Casanova I.; Hummel, L.; Kroupa, J. and Brezina, B., *Acta Cryst* **1990,** *B 46,* 830.

12. Ferraris, G.; Jones D. W. and Yerkess, J.,*Z. Kristallogr.* **1973,** *138,* 113.

13. Neidelen, R.; Christen. D.; Poignee, V.; Boese, R.; Blaeser, D.; Gieren, A.; Ruiz-Perez, C. and Huebner, T., *Angew. Chem. Intl. Ed. Engl.* **1988**, *27,* 294.

14. Blaeser, D.; Boese, R.; Brett, W.; Rademacher A.; Schwanger P.; Stanger, H. and Vollhardt, K. P. C., *Angew. Chem. Intl. Ed. Engl.* **1989**, *28,* 206.

15. Boese, R.; Blaeser, D.; Billups, E.; Haley, M. M; Maulitz A. H.; Mohler, D. L. and Vollhardt K. P. C., *Angew. Chem. Intl. Ed. Engl.* **1994**, *33,* 313.

16. Diercks, R. and Vollhardt, K. P. C., *J. Am. Chem. Soc.* **1986,** *108,* 3150.

17. Frank. N. L.; Baldridge, K. M. and Siegel, J. S., *J. Am. Chem. Soc.* **1995,** *117,* 2102.

18. Mills, W. H. and Nixon, I. G., *J. Chem. Soc.* **1930**, 2510.

19. Krygowski, T. M.; Anulewicz, R.; Jarmuła, A.; Bąk, T.; Rasała, D. and Howard, S.T., *Tetrahedron* **1994,** *50,*13155.

20. Howard, S. T.; Krygowski, T. M. and Główka, M. L. *Tetrahedron* **1996**, *52,* 11379.

21. Krygowski, T. M.; Anulewicz, R. and Hiberty, P. C., *J. Org. Chem.* **1996,** *61,* 8533.

22. Krygowski, T. M.; Howard, S. T.; Martynowski, D. and Główka, M., *J. Phys. Org. Chem.* **1997,** *10,* 125.

23. Krygowski, T. M.; Wisiorowski, M.; Howard, S. T. and Stolarczyk, L. , *Tetrahedron,* **1997**, *53,* 13027.

24. Krygowski, T. M.; Cyrański, M. and Wisiorowski, M. , *Pol. J. Chem.* **1996**, *70,* 1351.

25. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis M. and Montgomery. J. A., *J. Comput. Chem.* **1993**,.*14*, 1347.

26. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.;Nanayakkara, A.; Challacombe, M.; Peng, C.Y.; Ayala, P.Y.; Chen, W.; Wong, M. W.; Andres, J.L.; Replogle, E.S.; Gomperts, R.L.; Martin, R.L.; Fox, D.J. ;Binkley, J.S.; Defrees, D.J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C. and Pople, J.A. *Gaussian 94, Revision C.3* **1995**, Gaussian, Inc., Pittsburgh PA.

27. Biegler-König, F.W.; Bader, R.F.W.and Tang, T., *J. Comput. Chem.* **1982**, *3*, 317. These programs may be obtained from Prof. Bader, McMaster University, Hamilton, Ontario, Canada; e-mail: bader@ ca. mcmaster. cis.mcmail.

28. a) Krishnan, R.; Binkley, J. S. and Pople, J. A., *J. Chem. Phys.* **1980** ,*72*, 650.b) Hariharan, P. C. and Pople, J. A., *Theor. Chim. Acta* **1973**, *28*, 213. c) Frisch, M. J. and Pople, J. A.; Binkley, J. S., *J. Chem. Phys.* **1984**, *80*, 3265.

29. Hariharan, P. C. and Pople, J. A., *Theoret. Chim. Acta* **1973**, *28*, 213.

30. Bader, R. F. W.; Slee, T. S.; Cremer, D. and Kraka, E. ,*J. Am. Chem. Soc.* **1983**, *105*, 5061.

31. Krygowski, T. M.; Anulewicz, R. and Kruszewski, J. *Acta Cryst.* **1983**, B *39*, 732.