Pergamon

Tetrahedron 56 (2000) 8715–8719

TETRAHEDRON

Angular Group Induced Bond Alternation (AGIBA). Part 4: Does the Effect Operate in the Systems with Alternated Bonds?

Tadeusz M. Krygowski,[a,*] Edyta Pindelska,[a] Michał K. Cyrański[a] and Sławomir J. Grabowski[b]

[a]*Department of Chemistry, University of Warsaw, L. Pasteura 1, 02-093 Warsaw, Poland*
[b]*Institute of Chemistry, University in Bialystok, Al. J. Pilsudskiego 11/4, Poland*

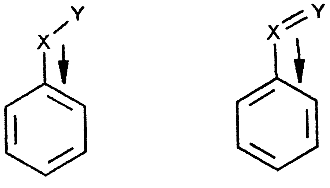
Received 20 April 2000; revised 18 August 2000; accepted 30 August 2000

Abstract—Angular groups attached to non-cyclic π-electron systems like amidine or 1,3-butadiene do not exhibit the AGIBA effect, whereas when attached to aromatic systems they act in an ambiguous way—the effect is much more local than in the cases observed in monocyclic systems (benzene, *s*-triazine). The above picture is based upon ab initio calculations at B3LYP/6-311+G** level of theory for 2,3,6,7- and 1,4,5,8-tetramethoxynaphthalene, 9,10-dimethoxyphenanthrene, 4,9- and 4,10-dinitrosopyrene derivatives of C_2 or *i* symmetry, and X-substituted 1,3-butadiene (X=NO, CHO, N=NH, CH=CH_2 and OCH_3) at B3LYP/6-31G* for C- substituted derivatives of formamidine substituted derivatives of formamidine (X=NO, CHO, N=NH, CH=CH2, OCH_3 and CH_2CH_3). © 2000 Published by Elsevier Science Ltd.

Introduction

Angular groups attached to π-electron delocalised ring(s) systems like benzene, *s*-triazine or phenalene cation, lead to an increase in the bond length alternation: the double bonded groups, –X=Y cause the elongation of the *cis* bond and a shortening of the *trans*-one, whereas –X–Y groups act in the opposite way: they elongate the *trans*-bonds and shorten the *cis* ones (Scheme 1).[1–5]

This effect has also been observed experimentally for ring systems with equalised bond lengths such as boraxine[6] and borazine.[7] Despite the bond length equalisation they are not considered as aromatic.[8–11]Additionally the observed effect may be treated as an illustration of the Hiberty–Shaik hypothesis.[12–14] Namely, that lack of bond alternation in benzene is not due to the π-electrons but to the σ framework, if AGIBA is considered to be not only due to rehybridisation but also due to π-electron interactions[3,4] between the bent substituent and the ring.



Scheme 1.

In the case of the π-electron systems in which bond alternation already does exist, the effect has not yet been studied except the case of 2,7,11,16-tetra-methoxyperylene with the C_2 symmetry.[15] In this case two different situations were considered: (i) when the methoxy group is oriented along the single bond (substitution in positions 2 and 11) and (ii) when the methoxy group is oriented along the double bond (substitution in positions 7 and 16). It was found that the effects observed in the *cis* bonds are very small whereas those in the *trans* bonds are substantially larger.

The purpose of this report is to answer the question formulated in the title: does the AGIBA effect work in the π-systems which already exhibit bond alternation?

Results and Discussion

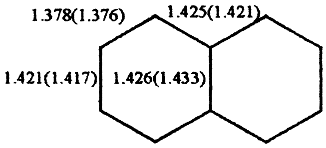
Three kinds of systems have been chosen: (i) aromatic systems like: naphthalene, phenanthrene and pyrene in which bond alternation already exists, (ii) non-cyclic derivatives of formamidine in which the π-electrons are delocalised in some of their dimers existing in the crystalline state[16] and hence may be expected to have some kind of an elastic π-electron system, and (iii) butadiene-1,3 which is a typical olefinic system. The model molecules were optimised at B3LYP/6-311+G** (i) and (iii) and B3LYP/6-31G** (ii).[17]

Aromatic systems

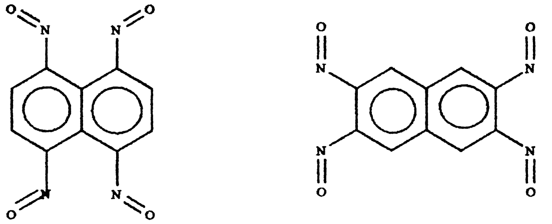
Aromatic systems, except benzene and some other monocylic systems usually have some kind of bond alternation.

Keywords: AGIBA effect; formamidine; angular groups; substituent effects.
* Corresponding author. Tel./fax: +48-22-8222-892;
e-mail: tmkryg@chem.uw.edu.pl

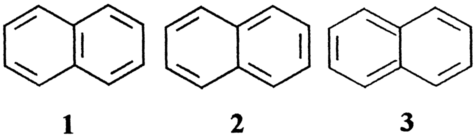
PII: S0040-4020(00)00799-7



Scheme 2. Naphthalene—experimental[18] and calculated at B3LYP/6-311+G** (in parenthesis) molecular geometry.



Scheme 3.



Scheme 4.

Naphthalene, phenanthrene and pyrene were chosen to study to what extent the angular groups affect the molecular geometry in the way expected by the AGIBA effect.

Naphthalene

Naphthalene has significantly alternated bond lengths (in Å) as shown in Scheme 2.

The AGIBA effect is composed of two contributions:[3] (i) the rehybridisation effect and (ii) π- electron interactions. In the case of single-bonded angular groups (like methoxy) it seems that the main effect is due to the changes in bond angle[3] and hence rehybridisation[19] is dominant.[3] In the case of double-bonded groups (like nitroso), both components of the AGIBA effect oppose each other: the rehybridisation vs π-electron interactions.[3] Therefore, for further studies, the double bonded-group (nitroso) was chosen as a substituent, as our interest is mainly focused on the π-electron nature of interactions.

Two kinds of substitution may induce the AGIBA effect: in both 1, 4, 5, 8- and in 2, 3, 6, 7-tetra-nitrosonaphthalenes (Scheme 3). The bonds 1,2; 3,4; 5,6 and 7,8 should become longer and the bonds 3,4 and 6,7-shorter.

In order to detect these changes in a numerical way the HOSE model[20,21] has been applied to calculate the weights of the canonical structures presented in Scheme 4.

Application of the HOSE model allows one to calculate the weights of the canonical structures for the whole naphthalene moiety as well as for a particular fragment. The global HOSE characteristics for 2,3,6,7- and 1,4,5,8-tetranitroso-napthalenes and the parent molecule are presented in Table 1.

A decrease in contribution of the canonical structure **1** should indicate that the AGIBA effect does work in these cases. Partial double bonds represented in the hybrid structures **2+3** by symmetrically equivalent bonds become longer and this leads to a significant change in a canonical structure distribution—to a decrease in weight of the canonical structure with double bonds as in structure **1**. Indeed, a small decrease in weight of the canonical structure **1** is observed. In order to check whether these changes are really due to the AGIBA effect and not to the electron-accepting property of the nitroso group, analogous computations were carried out for 1,4,5,8- and 2,3,6,7-tetra-cyanonaphthalenes, TCNN14 and TCNN23, respectively. Table 1 presents in the last two columns the results for cyano-substituted derivatives.

The decrease in weights of the canonical structure **1** is similar in both cases. This means that the AGIBA effect for the nitroso-substituted naphthalene is rather doubtful, at least from the viewpoint of the changes in molecular geometry of the whole molecule.

It is known that structural changes due to the topology of the rings fused to each other are very strong[22,23] thus the AGIBA effect which is energetically rather weak[15] may be masked. A typical analysis of the AGIBA effect performed by use of the HOSE model, was based on the whole-moiety canonical structures, and was very successful for monocyclic systems. In order to overcome the strong topological pattern of the molecular geometry, a more local treatment was proposed. Table 2 shows the canonical structures of the fragment of the naphthalene moiety directly associated with the substituted carbon atoms, omitting that part which is associated with the fusion of both rings.

If the AGIBA effect works, then the weight of canonical structure **III** should be decreased, since both double bonds should be elongated. This is fulfilled only in the case of 1,4,5,8 tetranitrosonaphthalene, when the weight for this canonical structure goes down to 66.9% whereas for all other cases it is over 80%. Since the AGIBA effect consists of a contribution from rehybridization of the substituted carbon atoms, the respective bond angles are given.

Table 1. Canonical structure weights (in %) for naphthalene (N) and its 2,3,6,7-tetranitroso-derivative (TNN23), 1,4,5,8-tetranitroso-derivative (TNN14), 2,3,6,7-tetracyanonaphthalene (TCNN23) and 1,4,5,8-tetracyanonaphthalene (TCNN14)

Structure/geometry	(N) Experimental[18]	(N) Theoretical	TNN23	TNN14	TCNN23	TCNN14
1	51.3	48.1	44.2	40.5	45.4	42.1
2+3	48.7	51.9	55.8	59.5	54.6	57.9

Table 2. Canonical structure weights for naphthalene (experimental value for naphthalene in brackets) and for 2,3- and 1,4-disubstituted derivatives

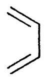
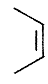
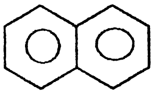
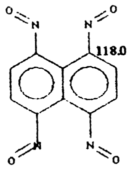
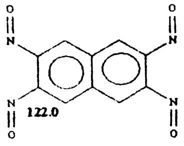
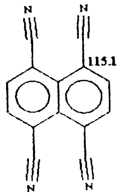
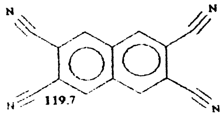
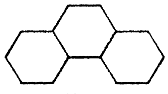
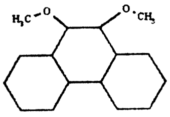
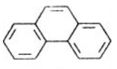
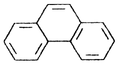
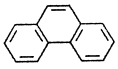
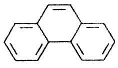
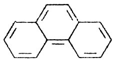
Compound	 (%) **III**	 (%) **IV**
	85.0 (82.0)	15.0 (18.0)
	66.9	33.1
	86.4	13.6
	88.5%	11.5
	87.0	13.0

Table 3. Canonical structure weights for phenanthrene and 9,10-dimethoxyphenanthrene

Canonical structures	 Exp.[20] (calcd)	 (%)
 **4**	22.4 (20.4)	19.4
 **5**	21.5 (20.4)	19.4
 **6**	22.0 (27.1)	26.7
 **7**	21.9 (16.4)	15.7
 **8**	12.2 (15.7)	19.3

Following computational experiments[3,19] the bond angle lower than 120° causes the C1C2 bond to be longer. However, a comparison of the angles for 1,4,5,8-tetranitroso- and 1,4,5,8-tetracyano-derivatives shows that in the case of the cyano derivatives there is no effect, whereas for the nitroso derivatives a large decrease in weight is observed. This can be taken as evidence that the AGIBA effect does works for 1,4,5,8-nitrosoderivative.

Phenanthrene

Another illustrative example is 9,10-dimethoxyphenanthrene (hereafter abbreviated DMP). Five canonical structures may be drawn for phenanthrene moiety (Scheme in Table 3), of which structure **8** is the one least representative for the unsubstituted moiety. In the case of DMP the situation changes dramatically. The 9,10 CC bond becomes significantly longer and hence the canonical structure **8** increases from 12.2% for the unsubstituted phenanthrene to 19.3% in DMP. The HOSE-calculated canonical weights are shown in Table 3.

In the case of DMP the methoxy groups work similarly as for o-dimethoxybenzene derivatives.[24] In this case a decrease in the double bond character of the 9,10 bond is observed and as a consequence an increase in weight of the canonical structure **8** with a single bond there. In the case of phenanthrene the AGIBA effect works, but mostly as an effect of rehybridisation.

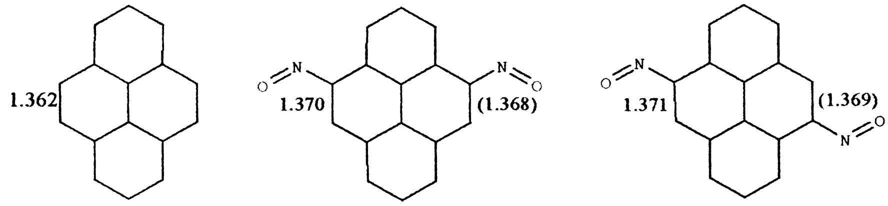
Pyrene

4,10- and 5,10-Dinitroso pyrene derivatives provide another illustration to the point that the AGIBA effect is observed very locally. The optimised geometry of pyrene and the above two derivatives shows that the double bond in pyrene moiety becomes longer when the nitroso groups are present, i.e. supporting the conclusion that the AGIBA effect works. The effect is rather local since due to the topological requirements the further part of the molecule does not follow the changes which are supposed to be caused by AGIBA (Scheme 5).

Formamidine derivatives

In the crystalline state formamidine derivatives form dimers in which, depending on the nature of substituent(s),[16] the π-electron skeleton may vary from the fully delocalised one to a fully localised structure, where the difference between CN bond lengths is as large as 0.078 Å.[16] Hence the π-electron structure may be assumed to be a rather mobile one, and it may therefore serve as a good model to study the AGIBA effect. To some extent it might resemble the benzene derivatives, in which the bond alternation appears even if the energetic effect is small.[15]

In this study, only the monomers of C-substituted formamidines were taken into consideration with the following substituents XY: NO, CHO, N=NH, $CH=CH_2$ and OMe. By analogy with our former studies the NCX angle was changed from the optimal one to the lower values by 5 and 10 degrees. In the case of 'classic' situations (benzene and *s*-triazine derivatives) these kind of changes (approaching



Scheme 5.

the XY group to the ring) always caused a significant increase of the difference between two subsequent bond lengths,[1,3]which may be a numerical measure of the AGIBA effect. The analysis of structural data for the C-substituted formamidines is carried out using the following criteria:

(i) analysis of the difference Δ_1 in bond length of the C–N and C=N bonds as compared with the value for unsubstituted formamidine. If the AGIBA effect dominates, the difference for the *cis* conformation of X=Y vs C=N should be smaller for X=Y substituents and larger for X–Y substituents.

(ii) analysis of the changes in CN bond lengths between the optimised structure CN(0°) and the one forced to have its NCX bond angle smaller by 10°, CN(10°). If the AGIBA effect dominates, the difference $\Delta_2=\{C{=}N\ (10°)\}-\{C{=}N\ (0°)\}$ for the *cis* conformer should be positive.

Since in the case of X–Y groups mostly the rehybridisation effect works,[4] in this analysis we concentrate on the X=Y substituents, where the π-electron interaction through space must outweigh the rehybridisation effect,[3,4] and hence results for these kind of substituents are more decisive. The results of these analyses are presented in Table 4.

As can be seen in Table 4, none of the requirements that would point to the existence of the AGIBA effect is present. Firstly, the Δ_1 values should be smaller for the X=Y substituents in conformation (B) than for formamidine itself. Secondly, the Δ_2 values should be positive for conformation B with the X=Y substituents. *It may thus be concluded that the AGIBA effect does not act in the π-electron skeleton of substituted formamidines.*

Additionally it is worth mentioning that much larger changes in bond length due to the change of conformation of the XY group by 10° are observed for the CX bond itself, numerically this is 5 to 10 times larger. This may be a sign that the mesomeric interactions between the amino and imino nitrogen atoms and the XY groups dominates over the AGIBA effect, which in principle is weak, whereas some of the XY substituents are more strongly electron accepting than the C=N group: σ for C=NPh=0.42, for CHO=0.47 and for N=O=0.65.[25] Nevertheless in the cases of benzene derivatives where the competition between AGIBA and mesomeric effects might appear, these two effects could be separated.[24]

Table 4. Differences are given in Å

Molecule/conformation	Δ_1	Δ_2	$\Delta_{2'}$
Formamidine	0.077		
Nitroso (A)	0.068	0.003	−0.001
(B)	0.087	−0.008	0.002
Formylo (A)	0.071	0.004	−0.002
(B)	0.087	−0.005	0.003
Diazo (A)	0.075	0.002	−0.002
(B)	0.085	0.001	0.000
Methoxy (A)	0.098	0.002	0.001
	0.088	−0.002	0.002

1,3-Butadiene-derivatives

Analysis of the planar, fully optimised geometry of 2,3-disubstituted 1,3-butadiene derivatives (XY: NO, CHO, N=NH, CH=CH2, OMe and CH_2CH_3 leads to the conclusion that in those cases AGIBA does not function at all. Most indicative here would be a change in length of the double bonds in these systems in the *cis* conformation to the XY groups. However, these changes are very small and mostly in the incorrect direction. For the fully optimised geometry, the C=C double bond lengths are: 1.319 Å for the NO derivative and 1.320 Å for N=NH. They are shorter than for OMe (1.325 Å) and CH_2CH_3 (1.324 Å) thus opposite to that required by the AGIBA effect. For the planar, constrained conformations the double bond lengths in these derivatives of 1,3-butadiene are (1.322 Å) and (1.322 Å), (1.326 Å) and (1.326 Å) respectively. In unsubstituted 1,3-butadiene the length of double bonds is of 1.322 Å. *Undoubtedly, the AGIBA effect is not observed in butadiene-systems.*

Conclusion

The results above-presented allow us to draw the following conclusions. If the angular groups are attached to non-cyclic π-electron systems, like formamidine or butadiene-1,3, then the AGIBA effect is not observed. If those groups are attached to the cyclic π-electron alternated systems (naphthalene, phenanthrene, pyrene) there are no unequivocal conclusions, but AGIBA usually works locally: partial double bonds become less double as predicted by the AGIBA model, but more distant parts of the molecule do not follow the requirements of the AGIBA effect. *A possible explanation of these rather local effects observed for polycyclic aromatic systems can be sought in the fact that strong topological requirements control molecular geometry and the AGIBA effect is too weak to overcome them.* The strengths of 'topological' enforcements in molecular geometry of polycyclic benzenoid hydrocarbons is well documented[22,23] and hence such an explanation can be treated a very probable hypothesis.

Acknowledgements

The KBN 3T09A 114 18 grant provided financial support for this study. Authors thank one of the Referees for very valuable help in preparing the final version of this paper.

References

1. Krygowski, T. M.; Anulewicz, R.; Jarmula, A.; Bak, T.; Rasala, D.; Howard, S. T. *Tetrahedron* **1994**, *50* (13), 155.
2. Howard, S. T.; Krygowski, T. M.; Glówka, M. L. *Tetrahedron* **1996**, *52* (11), 379.
3. Krygowski, T. M.; Anulewicz, R.; Hiberty, P. C. *J. Org. Chem.* **1996**, *61*, 8533.
4. Krygowski, T. M.; Wisiorowski, M.; Howard, S. T.; Stolarczyk, L. *Tetrahedron* **1997**, *53* (13), 027.
5. Krygowski, T. M.; Howard, S. T.; Martynowski, D.; Glówka, M. L. *J. Phys. Org. Chem.* **1997**, *10*, 125.
6. Boese, R.; Polk, M.; Blaser, D. *Angew. Chem., Int. Ed. Engl.* **1987**, *28*, 245.
7. Maulitz, A. H.; Stellberg, P.; Boese, R. *J. Mol. Struct.* **1995**, *338*, 131.
8. Boyd, R. J.; Choi, S. C.; Hale, C. C. *Chem. Phys. Lett.* **1984**, *112*, 126.
9. Haddon, R. C. *Pure Appl. Chem.* **1982**, *54*, 1129.
10. Jemmis, E. D.; Kiran, B. *Inorg. Chem.* **1998**, *37*, 2110.
11. Schleyer, P. v. R.; Jiao, H.; Eikemma, N. J. R. v.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119* (12), 669.
12. Shaik, S. S.; Hiberty, P. C.; Lefour, J.-M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363.
13. Shurki, A.; Shaik, S. S. *Angew. Chem. Int. Ed.* **1997**, *36*, 2205.
14. Shaik, S. S.; Shurki, A.; Danovich, D.; Hiberty, P. C. *J. Mol. Struct.* **1997**, *398*, 155.
15. Howard, S. T.; Krygowski, T. M.; Ciesielski, A.; Wisiorowski, M. *Tetrahedron* **1998**, *54* (3), 553.
16. Anulewicz, R.; Wawer, I.; Krygowski, T. M.; Maennle, F.; Limbach, H. H. *J. Am. Chem. Soc.* **1997**, *119*, 12223.
17. 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.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M. G.; Gonzalez, C. and J. A. Pople GAUSSIAN; Gaussian: Pittsburgh, PA, 1995.
18. Block, C. P.; Dunitz, J. D.; Hirshfeld, F. L. *Acta Crystallogr., Sect. B* **1991**, *47*, 789.
19. Stanger, A. *J. Am. Chem. Soc.* **1991**, *113*, 8277.
20. Krygowski, T. M.; Anulewicz, R.; Kruszewski, J. *Acta Crystallogr.* **1983**, *B39*, 732.
21. Krygowski, T. M.; Anulewicz, R.; Wisiorowski, M. *Pol. J. Chem.* **1995**, *69*, 1579.
22. Krygowski, T. M.; Cyranski, M.; Ciesielski, A.; Swirska, B.; Leszczynski, P. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 1135.
23. Cyranski, M.; Krygowski, T. M. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 1142.
24. Krygowski, T. M.; Piętka, E.; Anulewicz, R.; Cyranski, M. K.; Nowacki, J. *Tetrahedron* **1998**, *54*, 12289.
25. Exner, O. *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978, p 439.