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# Angular Group Induced Bond Alternation (AGIBA). Part VII. The Case of a Branched Substituent – the Carboxylic Group*

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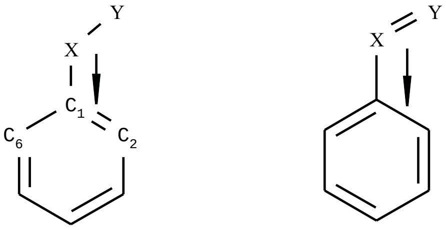
Angular groups attached to aromatic rings cause an increase of the double bond localization, called Angular Group Induced Bond Alternation (AGIBA). The effect for the groups with single bonds, X–Y, increases the double bond character of the *cis* CC bond in the ring, whereas the groups with double bonds, X=Y, work in the opposite way. The group with a *branched* structure, like the carboxylic one, should exhibit an enhancement of the AGIBA effect. Analyses of 61 geometries for p-substituted derivatives of benzoic acid, as well as of the geometry of benzoic acid optimized at B3LYP/6-311G** level of theory, show that there is no cooperative effect in this kind of substituent.

Key words: *ab-initio* calculations, benzoic acids, substituent effects, double bond localization

Angular groups substituted to the monocyclic π electron systems like benzene or *s*-triazine cause substantial structural consequences [1–4], known as the Angular Group Induced Bond Alternation (AGIBA) [5–7]. These effects, documented by both the experimental and computational studies [1–7], may be briefly presented by 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, like benzene or *s*-triazine, and are also observed in non-aromatic systems, like borazine and boraxine [8,9]. Usually the effect is described either by the difference between the $C_1C_2$ and $C_6C_1$ bond lengths, or by using the HOSE model [10,11], which

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* Dedicated to the memory of Professor Krzysztof Pigoń.

allows us to estimate the weights of the canonical structures directly from the bond length of a molecule or its fragment in question. Then the imbalance between two Kekule structures of benzene manifests the AGIBA effect. For benzene derivatives the Kekule structure imbalances for the whole ring and solely for the $C_1C_2$ and $C_1C_6$ bonds are practically the same [4]. The mechanism of the above described changes in geometry is composed of two effects [4,5]: (i) A sigma electron one, being due to the rehybridization at the substituted carbon, which according to the Bent-Walsh rule [12,13], results from the increase of the bond angle $XC_1C_2$, which in consequence increases the s-contribution to the $sp^2$ orbital in the direction of the $C_1C_2$ bond and makes the bond shorter. This is well known for benzene annealed with small rings and is often associated with the Mills-Nixon effect [14]. Recently, it has been nicely documented by X-ray determined structures [15] and also analyzed by computational experiments [16–20]. (ii) A through space $\pi$ electron interaction between the double bonds in the X=Y group and the $C_1C_2$ bond in the ring, leading to the lengthening of the latter bond [4]. This effect is considerably stronger than (i) and shows that in spite of the fact that the $XC_1C_2$ bond angle is larger than 120° (and in principle similar as those for X–Y substituted species) the $C_1C_2$ bond is longer than $C_1C_6$ [5]. It might be concluded from Scheme 1 that in the case of a branched group, like the carboxylic one, which consists of two angular sub-groups: the X=Y type (the carbonyl) and the X–Y type (the COH group), the AGIBA effect should be enhanced, since both these groups work in line. The CO group should lengthen the $C_1C_2$ bond and shorten the $C_1C_6$, in the same way as the COH group, which should make $C_1C_6$ shorter and $C_1C_2$ longer.

The purpose of this paper is to answer the question, whether or not the abovementioned enhancement appears. p-Substituted benzoic acid derivatives are chosen for this purpose, since there is a reasonably large amount of well done X-ray structures archieved in CSD [21]. Additionally a high level *ab-initio* optimization of benzoic acid was carried out, in order to have a precise geometry of the molecule examined without being perturbed by the adjacent molecules in the crystal lattice. As it is known, exocyclic bond angles may be readily deformed by these kind of interactions [22].

## RESULTS AND DISCUSSION

Molecular geometry of 61 p-substituted derivatives of benzoic acid were retrieved from CSD and analyzed. The choice of the p-substituted derivatives results from the recently documented fact [23] that the p-substituents, even if strongly interacting with the counter-substituent, do not reduce the AGIBA effect in any significant way. Moreover, the carboxylic group is known as a not too strong electron-accepting substituent [24], and hence the p-substituted benzoic acids are the best group of systems for studying the title problem. The mean bond lengths calculated for $C_1C_2$ and $C_1C_6$ bonds are 1.3882 Å and 1.3881 Å, respectively. Thus, the difference between these two values is meaningless. The mean bond angles calculated for $C_7C_1C_2$ and

$C_7C_1C_6$ angles are 121.13° and 119.68°, respectively. The Student test [25] defines the difference between these two values as significant at $\alpha = 0.01$. This means that the rehybridization effect should operate and the $C_1C_2$ bonds should become shorter. This is not observed. Fig. 1 presents scatter plots of $C_1C_2$ and $C_1C_6$ bond lengths plotted against $C_7C_1C_2$ and $C_7C_1C_6$ bond angle for the whole sample.

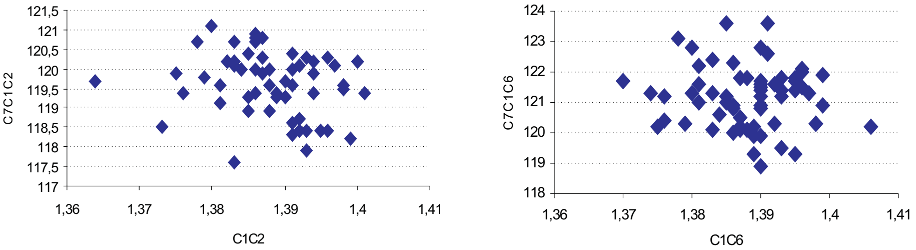
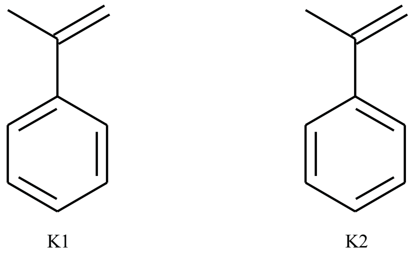


Figure 1. Scatter plots of $C_7C_1C_2$ and $C_7C_1C_6$ bond angles against $C_1C_2$ and $C_1C_6$ bond lengths for 61 p-substituted derivatives of benzoic acid.

Application of the whole ring geometry and using the HOSE model [10,11] does not change the result. The imbalance between two Kekule structures K1 and K2 (Scheme 2) is 50.17%:49.83% far below any significance.

Scheme 2



One could claim that most carboxylic acids dimerize in the crystalline state, [26] however, from the point of view of crystallographic measurements the H-bonds in these systems are usually weak, leading only to a subtle CO lengthening and COH shortening. Hence, they should not influence the appearance of the AGIBA effects. However, it should be added here, that the solid state NMR studies and quantum chemical calculations bear a somewhat different picture: in some cases the dynamics of protons is found or is expected in the carboxylic acid dimer [27]. However a similar system, the cyclic N,N′-bisarylformamide dimers studied by the combined X-ray diffraction and $^{15}$N CPOMAS NMR techniques between 100–300 K, revealed that the disorder observed in NMR measurements are associated with an equalization of C–N and C=N in the amidine skeleton [28]. In order to consider the problem as free from additional interactions, like intermolecular interactions in the crystalline state or intramolecular ones due to a substitution, we have computed optimized geometry of benzoic acid, benzylic alcohol and benzoic aldehyde.

It results from the above-presented geometries that the formyl group causes a weak AGIBA effect, since the $C_1C_2$ bond is longer than $C_1C_6$ by 0.003 Å. Similarly the $CH_2OH$ group causes a weak effect in the same direction: $C_1C_2$ bond is longer than $C_1C_6$ by 0.003 Å. Since it is known that the AGIBA effect works in an additive way [29], one could expect that the COH and CO groups in the carboxylic group should co-operate, leading to an enhancement of the effect in the PhCOOH. However, the geometry pattern of PhCOOH does not support this expectation. The $C_1C_2$ bond length is equal to that of $C_1C_6$ (1.402 Å). The whole ring effect described by the imbalance of the Kekule structures is also ambiguous: 50.86%:49.14% is very similar to that for a statistical mean structure obtained from X-ray data: 50.2%:49.8%. In contrast to that, the Kekule structure imbalance for PhCHO and $PhCH_2OH$ follows the local and the whole ring estimations of the AGIBA effect, which are 53.6%:46.4% and 52.5%:47.5%, respectively. The molecule of PhCOOH, PhCHO and $PhCH_2OH$ optimized by use of DFT at B3LYP/6-311G** level of theory applying Gaussian 94 [30] are planar with the geometry shown in Fig. 2.

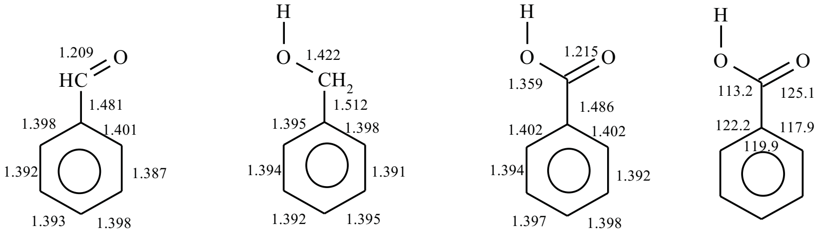


Figure 2. Molecular geometry (bond lengths) of benzoic aldehyde, benzylic alcohol and benzoic acid (both: bond lengths and bond angles).

The exocyclic bond angles at C1 in benzoic acid differ remarkably, they are 122.2° (under COH) and 117.9 ° (under C=O). According to the Bent-Walsh rule, the $C_1C_6$ bond should become shorter. This effect should be even enhanced by the through space $\pi$ electron interaction from the C=O group of the carboxylic group. Nothing like this is observed – both $C_1C_2$ and $C_1C_6$ are of the same lengths.

The analyses of the experimental data for 61 p-substituted benzoic acid derivatives, as well as of the theoretically computed geometry for benzoic acid as well as for benzylic alcohol and benzoic aldehyde, lead to the same conclusion, namely that the C–O and C=O groups work in the alcohol and aldehyde, but in the carboxylic group they do not cooperate in terms of the AGIBA effect.

Note added in proof: Optimized geometry of the benzoic acid dimer at B3LYP/6-311G* level of theory gave $C_1C_6$ and $C_1C_2$ bonds of the same length equal to 1.400 Å indicating no AGiBA effect. The energy of the hydrogen bond is –11.1 kcal/mole taking into account the basis set superposition error.

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## REFERENCES

1. Krygowski T.M., Anulewicz R., Jarmuła A., Bąk T., Rasała D. and Howard S.T., *Tetrahedron*, 50, 13155 (1994).
2. Howard S.T., Krygowski T.M. and Główka M.L., *Tetrahedron*, 52, 11379 (1996).
3. Krygowski T.M., Howard S.T., Martynowski D. and Główka M.L., *J. Phys. Org. Chem*, 10, 125 (1997).
4. Krygowski T.M., Anulewicz R. and Hiberty P.C., *J. Org. Chem.*, 61, 8533 (1996).
5. Krygowski T.M., Wisiorowski M., Howard S.T. and Stolarczyk L.Z., *Tetrahedron*, 53, 13027 (1997).
6. Howard S.T., Krygowski T.M., Ciesielski A. and Wisiorowski M., *Tetrahedron*, 54, 3533 (1998).
7. Krygowski T.M., Pindelska E., Cyranski M.K. and Grabowski S.J., *Tetrahedron*, 56, 8715 (2000).
8. Boese R., Polk M. and Blaser D., *Angew. Chem. Int. Ed. Engl.*, 28, 245 (1987).
9. Maulitz A.H. Stellberg P. and Boese R., *J. Mol. Struct.*, 338, 131 (1995).
10. Krygowski T.M., Anulewicz R. and Kruszewski J., *Acta Cryst.*, B39, 732 (1983).
11. Krygowski T.M., Anulewicz R. and Wisiorowski M., *Polish J. Chem.*, 69, 1579 (1995).
12. Walsh A.D., *Disc. Farad. Soc.*, 2, 18 (1947).
13. Bent H.A., *Chem. Rev.*, 61, 275 (1961).
14. Mills W.H. and Nixon I.G., *J. Chem. Soc.*, 2510 (1930).
15. Boese R., Blaeser D., Billups W.E., Haley M.M., Maulitz A.H., Mohler D.L. and Vollhardt K.P.C., *Angew. Chem. Int. Ed. Engl.*, 33, 313 (1994).
16. Stanger A., *J. Am. Chem. Soc.*, 113, 8277 (1991).
17. Maksić Z.B., Eckert-Maksić M., Hodoscek M., Koch W. and Kovacek D., in *Molecules in Natural Science and Medicine*, Maksić Z.B. and Eckert-Maksić M., (Eds.), Ellis Horwood, Chichester, 1991, p. 334.
18. Siegel J., *Angew. Chem. Int. Ed.*, 33, 1721 (1994).
19. Koch W., Eckert-Maksic M. and Maksic Z.B., *Int. J. Quant. Chem.*, 48, 319 (1993).
20. Stanger A., *J. Am. Chem. Soc.*, 120, 12034 (1998).
21. Allen F.H., Bellard S., Brice M.D., Cartwright B.A., Doubleday A., Higgs H., Hummelink T.W.A., Hummelink-Peters B.G.M.C., Kennard O., Motherwell W.D. S., Rodgers J.R. and Watson D.G., *Acta Cryst.*, B35, 2331 (1979).
22. Bernstein J., in *Accurate Molecular Structures – Their Determination and Importance*, A. Domenicano and I. Hargittai, (Eds.), Oxford University Press, 1992, p. 489.
23. Pindelska E., Krygowski T.M., Anulewicz R., Cyrański M.K. and Nowacki J., *J. Phys. Org. Chem.*, in press.
24. Exner O., in *Correlation Analysis in Chemistry – Recent Advances*, Chapman N.B. and Shorter J., (Eds.), Plenum Press, London, 1978, p. 439.
25. Cochran W.G. and Snedecor G.W., *Statistical Methods*, The Iowa State University Press, Ames, 1973, p. 59.
26. Leiserowitz L., *Acta Cryst.*, B32, 775 (1976).
27. Chojnacki H., this issue, *Polish J. Chem.*, 76, 295 (2002) and references therein.
28. Anulewicz R., Wawer I., Krygowski T.M., Mannele F. and Limbach H.-H., *J. Am. Chem. Soc.*, 119, 12223 (1997).
29. Krygowski T.M., Pindelska E., Anulewicz-Ostrowska R., Grabowski S.J. and Dubis A., *J. Phys. Org. Chem.*, 14, 349 (2001).
30. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Robb MA, Cheesman JR, Keith T, Peterson GA, Montgomery JA, Raghavachari K, Al-Laham MA, Zakrzewski VG, Ortiz JV, Foresman JB, Cioslowski J, Stefanov BB, Nanayakkara A, Challacombe M, Peng CY, Ayala PY, Chen W, Wong MW, Andres JL, Replogle ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, Defrees DJ, Baker J, Stewart JP, Head-Gordon M, Gonzales C, Pople JA, *Gaussian 94*; Gaussian inc. Pittsburgh PA, 1995.