

Separation of the Energetic and Geometric Contributions to Aromaticity. 3. Analysis of the Aromatic Character of Benzene Rings in Their Various Topological and Chemical Environments in the Substituted Benzene Derivatives

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Molecular geometry of 2045 rings of all kinds of the substituted benzene derivatives enabled estimation of their index of aromaticity HOMA and its components GEO and EN (geometric and energetic contributions, respectively). It is shown that the benzene ring in substituted derivatives loses its aromatic character to a much smaller extent than in the case where it is embedded in benzenoid hydrocarbons. In all cases of substituted benzene derivatives dearomatization due to substitution is mostly due to the geometric term.

Aromaticity is one of the most fundamental concepts in organic chemistry and has been defined in many various ways.^{1–3} Recently the problem of multidimensionality of this term has been vividly discussed.^{4–8} Benzene ring is a paradigm for the definition of aromaticity, and hence its behavior in dependence on the nature of the closest environments is of great interest. It has been shown that depending on the topological environments in benzenoid hydrocarbons, the benzene ring may change its aromatic character from the almost nonaromatic to the fully aromatic ones.⁶ Moreover, it was shown in our previous paper⁹ that dearomatization of a particular ring may result from two factors: (i) either it is due to an increase in alternation of bond lengths (geometric factor) or (ii) it is due to a decrease in resonance energy of this ring (energetic factor). Owing to the recently published method enabling numerical estimations of these factors from bond lengths,¹⁰ two important regularities have been shown.⁹ If the ring in question is fused to three or less than three other rings, the dearomatization is due mostly to the geometric factor, whereas for the rings to which four or more other rings are fused, the dearomatization is due mostly to the energetic factor.

The aim of this paper is to investigate the influence of the closest environment on the aromatic character of the given ring in the case of substituted derivatives of benzene. By comparison of these data with those obtained for the rings perturbed by (almost) purely topological effects, as it is realized in the case of benzenoid hydrocarbons, one may find the effect exerted by the chemically modified topological environment on the aromatic character of a given ring. Such modifications are realized by changes of the closest chemical environment by virtue of the variation of the number, positions, and nature of substituents.

RESULTS AND DISCUSSION

The subject of our analysis is based on molecular geometry of the ring of 2045 substituted benzene derivatives retrieved from CSD.¹¹ The sample is divided into 12 subsamples, as shown in Chart 1. Only precise X-ray neutron diffraction data ($As = 1$ and $RFAC < 0.1^{11}$) were taken into account. The substituents selected for this study could not contain,

on average, more than three carbon atoms per one position of substitution, with no limitation for atoms of other elements. No heavy metal complexes and no complexes were taken into study. The HOMA, EN, and GEO values are calculated applying formulas 3–5b of part 2 of this series.⁹

Chart 1 presents median values¹² of HOMA, EN, and GEO indices for 12 groups of differently substituted benzene rings, labeled in column 2. To each of these groups may be associated appropriate groups defined for the case of benzene rings embedded in the benzenoid hydrocarbons,⁹ labeled in column 8. In a few cases there is no equivalence between those two kinds of classification, but in spite of this some conclusions may be drawn.

In all cases of the studied sample, the decrease in the aromatic character of the benzene ring in question caused by the substituent effects is significantly smaller than in the case of benzene rings in benzenoid hydrocarbons. The observed differences in their median values of HOMA are considerable. As a rule they are the greatest for the cases with more benzene rings fused to the ring in question (groups VII, IX, X, and XI in classification⁹).

In all cases of the substitution effects on the aromatic character of the benzene ring, the dominant contribution to dearomatization is due to the geometric term.











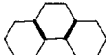



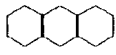

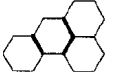
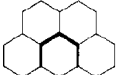

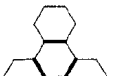
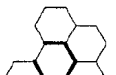
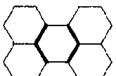
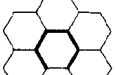
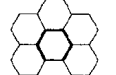
Except in a few cases (groups 8, 11, and 12), the energetic effect is completely negligible. It is worth mentioning that respective rings in the benzenoid series (groups IV and VII–XII) exhibit a dominant contribution of the energetic term.

The above conclusions are nicely illustrated by Figures 1–3, in which median values of HOMA, EN, and GEO are plotted against the number of substituents attached to the ring. These scatter plots show a rather large dispersion. However, if the case (5) is excluded as an exemption, then the relationships become much better.

Both least-squares lines for EN and GEO against the number of substituents have positive slopes, i.e., an increase in the number of substituents is associated with an increase in dearomatization of the ring. The slopes for EN and GEO vs the number of substituents are 0.0029 and 0.0036, respectively. This means that GEO terms are more sensitive to the variation of the number of substituents, i.e., roughly on the magnitude of perturbation than EN terms. An

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Chart 1

Type of ring	Class	Sample size	HOMA	EN	GEO	Group	Class	HOMA	EN	GEO
	1	126	0.994	-0.00503	0.0135					
	2	379	0.973	-0.00003	0.0297		I	0.862	0.00928	0.128
	3	34	0.993	-0.00379	0.0126					
	4	326	0.990	-0.00331	0.0143					
	5	217	0.866	0.00561	0.115		II	0.821	0.0361	0.141
	6	312	0.975	-0.00035	0.0247					
	7	22	0.995	-0.00016	0.00587					
	8	108	0.937	0.00623	0.0572		III	0.503	0.134	0.329
							V	0.639	0.155	0.192
	9	154	0.964	0.0014	0.0335					
	10	119	0.966	0.0014	0.0295		IV	0.818	0.124	0.0574
	11	87	0.946	0.0098	0.0390		VI	0.645	0.146	0.164
							VIII	0.794	0.157	0.0531
	12	161	0.967	0.0078	0.0218		VII	0.314	0.484	0.202
							IX	0.271	0.549	0.192
							X	0.219	0.662	0.0722
							XI	0.459	0.436	0.0845
							XII	0.728	0.212	0.0599

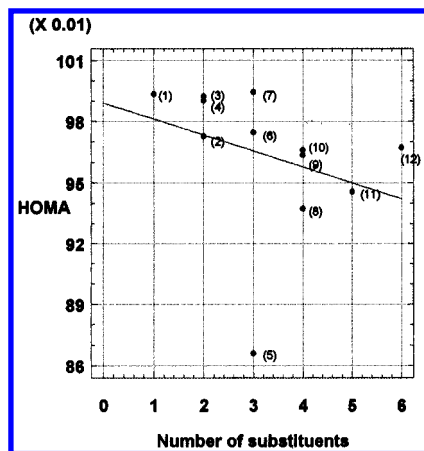


Figure 1. Plot of median values of HOMA against a number of substituents.

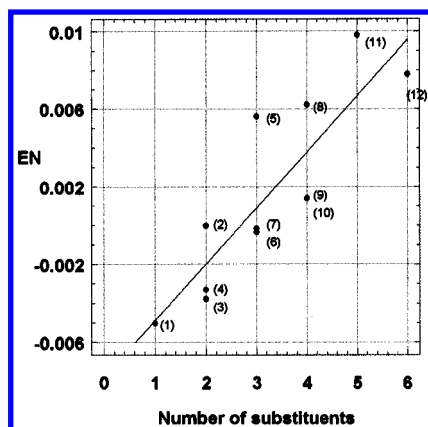


Figure 2. Plot of median values of EN against a number of substituents.

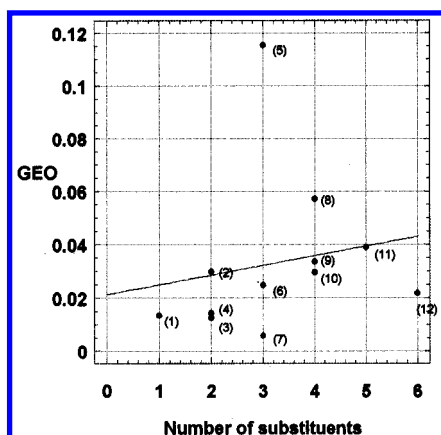


Figure 3. Plot of median values of GEO against a number of substituents.

interesting regularity has been observed for a group of subsamples with an increased number of ortho substituents: (2), (5), (8), and (11). For this group an approximate linear dependence is observed for the plot of EN vs the number of substituents. These subsamples exhibit always the highest effect of dearomatization. In consequence the overall aromaticity of subsamples of this group is always the lowest. The (5) subsample is a strange case: it has the lowest HOMA and a very high EN values, but the decisive term in determining its low aromaticity is GEO. After adding next ortho substituents to (5) group, the aromatic character of these subsamples increases, mainly due to the GEO term. An interesting finding is that the meta-type substituted deriva-

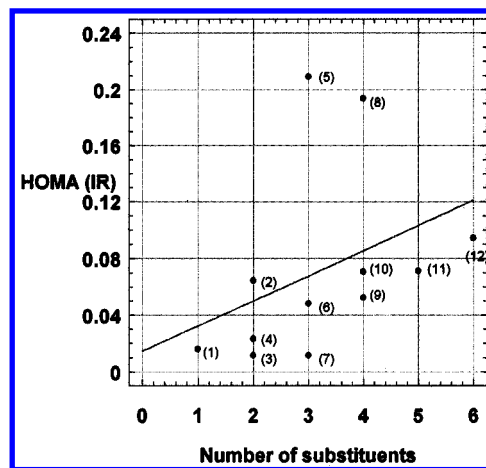


Figure 4. Plot of interquartile range of HOMA against a number of substituents.

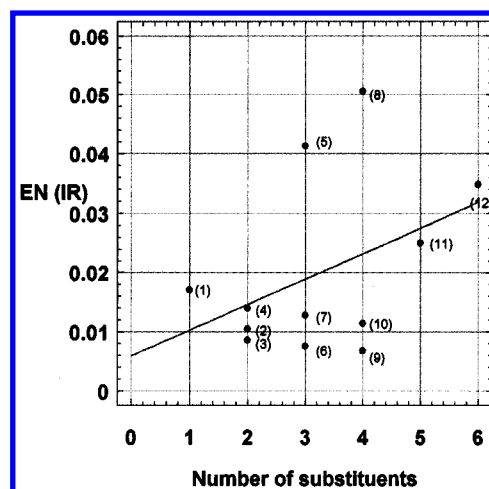


Figure 5. Plot of interquartile range of EN against a number of substituents.

tives (3) and (7) exhibit the highest aromatic character for the subsamples with two- and three-substituted benzene rings. This may be explained by the well-known fact of the low contribution of resonance effects for these kind of substituted species. In *m*-nitroaniline or similar systems the distortions of bond lengths from the mean values are definitely smaller than in the case of para analogues,^{13–15} in which resonance effects operate much stronger.

The dispersions of variation of these two contributions described by interquartile ranges (IR) differ significantly. The slopes of IR vs the number of substituents for EN and GEO are 0.0043 and 0.0091, respectively, as shown in Figures 4–6, and vary in line with the changes of median values.

Thus the dominant contributions determining the changes in overall aromatic character described by HOMA are those coming out from variation of GEO terms. The aromatic character, in general, decreases with an increase in the number of substituents attached to the ring.

There is a fundamental difference between the two kinds of perturbation affecting the molecular geometry of the benzene ring in the two samples discussed here. In the case of benzenoid hydrocarbons (groups I–XII) various topological environments of the given ring are built up always of sp^2 hybridized carbon atoms or hydrogen atoms. Thus the difference in electronegativity between these two kinds of atoms is rather low and equals 2.48 and 2.20.¹⁶ The long-distance effects of environment seem to play an important

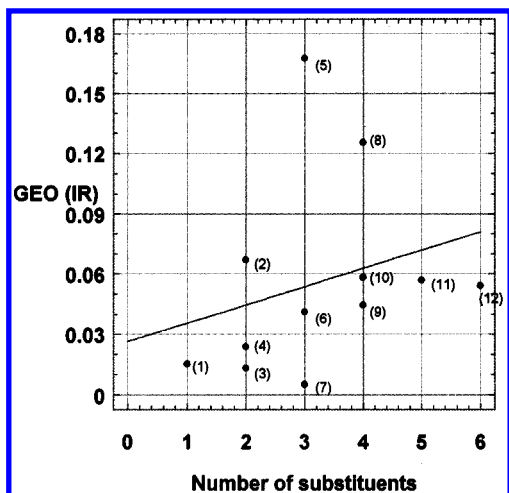


Figure 6. Plot of interquartile range of GEO against a number of substituents.

role in these systems. This is well visualized by much greater values of interquartile ranges for benzene rings in benzenoid hydrocarbons with many fused rings than it is observed for equivalently substituted rings in the benzene derivatives.

In the case of substituted derivatives the attached substituents may differ significantly in their electronegativity, and, moreover, strong resonance effects may function in and through the ring. In spite of this, the median values of HOMA for the benzene rings in question are, except one case (5), always greater than 0.93. Thus the loss of aromatic character due to the substituent effect is much lower than that due to the (almost purely) topological environment of the ring in question.

ACKNOWLEDGMENT

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