Structural Consequences of the Substituent Nonsymmetry on the Geometry of the Benzene Ring. Analysis of the Molecular Geometry of Diazo-Derivatives of Benzene

Tadeusz M. Krygowski,*[,†] Romana Anulewicz,[†] and Philippe C. Hiberty[‡]

Department of Chemistry, University of Warsaw, ul. Pasteura 1, 02 093 Warsaw, Poland, and the Laboratoire de Chimie Theorique, Bat 490, Universite de Paris-Sud, 91 405 Orsay Cedex, France

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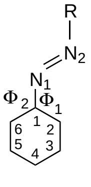
Analysis of the precisely measured geometry (retrieved from the CSD) of 21 diazobenzene derivatives revealed that the CC bond in the ring *cis* to N═NR group is significantly longer than the *trans* CC bond. This effect is propagated over the whole ring, resulting in the imbalance of two Kekule structure weights equal to 54.8:45.2 for the mean geometry. 6-31G* calculation of 1,3,5-tridiazabenzene in C_3 symmetry shows the substantial enhancement of the effect. Approaching the N═NH group to the C1C2 bond of the ring by bending the CNN bond and keeping the C2C1N angle fixed enhanced the effect considerably. By rotation around the C1N bond to the perpendicular conformation and keeping the C2C1N bond angle fixed, the π electron interactions are removed and the effect observed is due mostly to the strain. It is opposite to that of the optimized planar conformer. The conclusion is that the imbalance of Kekule structures for a ring is due to the combination of the strain effect and the π electron interaction of the diazo group with the ring.

Bond alternation in substituted benzene is generally observed whenever the aromatic ring is fused to one or several small rings[1−8] and is generally interpreted as the consequence of an imbalance between the weights of the two Kekule structures, following the original Mills−Nixon postulate.[1] Such bond fixation has been shown to arise from a combination of angular strain and perturbation of the aromatic π system by hyperconjugation with the fused rings.[6,7] Although angular strain alone has been shown to be sufficient to cause bond fixation,[6] it has been noted, in the case of benzenes fused to four-membered rings, that the principal source of bond alternation is either hyperconjugation or conjugation.[7] Open substituents are not generally known to induce bond fixation. However, we have recently observed[9] in a computational experiment that the methoxy group in anisole causes slightly unequal weights of the two Kekule structures with the ratio 52.6:47.4, an observation further supported by the experimental geometry of 1,3,5-trimethoxybenzene.[10,11] Now since the Mills−Nixon effect seems to be much magnified in annelated benzenes when the fused rings are themselves unsaturated, one may wonder if unsaturated open substituents, rather than fused rings, might induce a clearly observable bond alternation in the benzene ring. This paper addresses this extension of the original Mills−Nixon effect. We have chosen for this study diazo-derivatives of benzene for two reasons: (i) the diazo-group is a nonsymmetrical substituent, and (ii) in the Cambridge Structural Database[12] there was a sufficient number of precisely solved crystal structure with AS = 1 (i.e., with mean esd for bond lengths less or equal to 0.005 Å). For this study, 16 entries retrieved from CSD were enriched by the data from our laboratory for four diazobenzene derivatives.[13,14]

Chart 1



The following structural parameters (Chart 1) were used in our analysis: all CC bond lengths in the ring, both exocyclic bond angles at the ipso carbon atom, ϕ_1 and ϕ_2, and the torsion angle C2C1N1N2, τ, which was used to identify orientation of the diazo-group in relation to the ring. Bond lengths were used for calculating weights of the Kekule structures K_1 and K_2 and K'_1 and K'_2 (Chart 2).

[†] University of Warsaw.

[‡] Universite de Paris-Sud. Associated with the CNRS, URA 506.

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(10) Stults, B. R. *Cryst. Struct. Commun.* **1979**, *8*, 401. Due to the very low precision of the molecular geometry determination of 1,3,5-trimethoxybenzene, this support is weak. The redetermination was done at low temperature with high precision (ref 11) and fully supported the alternation of bond lengths due to the methoxy group.

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(14) In some cases two independent molecules in the crystal lattice existed.

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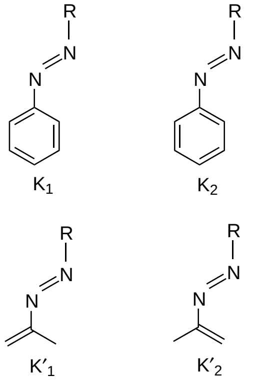
Chart 2



Analysis of the above-mentioned structural data for 21 diazo-derivatives of benzene[14] (Table 1) leads to the important findings.

The difference between the mean values of ϕ_1 and ϕ_2 is significant and amounts to 9.6°, indicating the substantial interactions between the hydrogen atom C2H in the ring and N2 of the diazo group. The difference between the mean bond lengths *d*(C1C2) and *d*(C6C1) for the sample in Table 1 amounts to 0.0066 Å. In order to test statistically how significant this difference is, the Student's *t* test was used.[15] The difference was significant at both commonly accepted significance levels $\alpha = 0.05$ and $\alpha = 0.01$. The above procedure assumes the normality of the data distribution, which could not be tested reliably due to the small number of data. Therefore, the nonparametric tests were also applied, which are free of any assumption regarding distribution of the variable in question.[16] Three tests were used for this purpose: tests based on signs, on ranks, and on pairs. All of them said the same: the difference is significant at both $\alpha = 0.05$ and $\alpha = 0.01$ significance levels. This statistically rigorous result is well supported by the apparent finding that only in two cases of the total 21 was it found that *d*(C1C2) < *d*(C6C1) and in two cases that these lengths were equal to each other. Moreover, these deviating differences were very low: 0.002 and 0.003 Å. The experimental differences depend roughly on the value of the dihedral angle C2C1N1N2: the differences decreased with an increase of the absolute value of the angle.

These findings need interpretation. The mean torsion angle τ equals 9.6°, which together with an increased mean value of $\phi 1$ support the view that the interactions between the hydrogen atom at C2 in the ring and the lone pair at N2 in the diazo group are not attractive.

More complex is the problem of the lengthening of C1C2 bond in comparison to that of the C6C1 bond. This effect is even better illustrated by considering mean weights of the Kekule structures K_1 and K_2 (Chart 2) calculated from bond lengths by use of the HOSE model.[17] They are 54.8 and 45.2%, respectively, if only C1C2 and C6C1 bonds are taken into account (K′ structures in Chart 2). Thus, the diazo group induces an increased localization of the π-electron structure, which in the language of Kekule structure contributions means unequality of K'_1 and K'_2. If the whole ring geometry is taken into account by the HOSE model, then K_1 and K_2 are equal to 54.2 and 45.8%, respectively. Note that the picture did not change. It means that even a slight localization of π electrons at this bond is effectively propagated onto the whole π electron system of the ring.

In order to better understand the observed experimental phenomena, we have carried out Hartree–Fock calculations 6-31G* for diazobenzene and 1,3,5-tridiazobenzene of C_3 symmetry. Both of them were planar. Applying the HOSE method[17] to the optimized geometry (bond lengths), we found for the tridiazo derivative a very significant imbalance between the two Kekule structures, with a K_1/K_2 ratio of 66.5:33.5. Thus, the observed experimental effect increases if the diazo groups are in 1,3,5-positions, each group enhancing the localization of the π electron structure, leading to the large overall effect. Following the first observation of this kind[9] that changes of COC angle in anisole cause variations in localization of the π electron structure and unequality of weights of the two Kekule structures, we have carried out calculations on 1,3,5-tridiazobenzene with C_3 symmetry, bending the NNC bond angle from 100° to 120° by 4° but keeping fixed C2C1N and C1C2H angles as those in the fully optimized structure, i.e., keeping them at 123.87° and 120.62°, respectively. This way, we freeze the angular strain of the substituents, so that the observed changes in geometry only (mostly) result from direct interactions between π electrons. The results are shown in Table 2. The structural consequences on bond lengths are dramatic. In language of Kekule structures the weights vary from $K_2 = 33.48\%$ for the optimal geometry (and 33.88% for the NNC angle = 120°) to 26.51% for the NNC angle = 100°. It is thus clear that approaching the N═N group close to the ring reinforces the bond alternation by disfavoring the Kekule structure that bears C═C and N═N facing each other. This can be explained by a tendency of the electronic system to avoid antiaromatic situations as is observed in benzene fused to unsaturated rings.[8]

Other facts or computational experiments reinforce this interpretation. Thus, the direct π-electronic interactions between the N═N groups and the ring can be eliminated by rotating these groups by 90° around their C–N bonds, leaving all other geometrical parameters unchanged, except the ring bond lengths that are reoptimized. In such a constrained molecule, any distortion of the ring must be solely due to the angular strain induced by C2C1N and C1C2H angles, which remain fixed at 123.87° and 120.62°, respectively. As a result, the ring still undergoes an important bond alternation (C1–C2 = 1.3753 Å, C1–C6 = 1.3916 Å), but in a way *opposite* to that observed in the planar tridiazo derivative. In the same line, it is interesting to note that trimethoxybenzene,[11] which also undergoes angular strain but (almost) no direct π electronic interactions, behaves like the rotated tridiazobenzene with a C1–C6 larger than C1–C2. Similar bond alternations due to angular strain have been computationally observed by Stanger[6] in a constrained bent benzene; as the HCC are varied from 120° to 90° in a C_3 geometry, the CC bonds that are between the small HCC angles are longer than the others. All these results point to the same conclusion: the bond alternation induced by angular strain is opposite to that induced by direct π electronic interaction in tridiazoben-

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Table 1. Structural Data of Diazobenzene Derivatives Retrieved from CSD (AS = 1, Release April 1995) and Determined in Our Laboratory (Last Five Lines[13]) ($\phi 1$,$\phi 2$, and τ = (C2C1N1N2 + C6C1N1N2)/2 Defined in Chart 1, K_1 and K'_1 Defined in Chart 2)

ref code	$\phi 1$	$\phi 2$	τ	*d*(C1−C2)	*d*(C1−C6)	K_1	K'_1
AZOBENO1[a]	124.1	115.5	15.3	1.385	1.384	58.5	50.8
	126.9	112.7	−5.8	1.383	1.373	56.6	57.3
AZOBENO3[b]	123.7	115.6	16.0	1.389	1.387	52.6	51.6
CETMIX[c]	125.2	114.6	20.0	1.378	1.367	53.2	57.5
GARSIB[d]	125.1	114.8	7.0	1.376	1.375	54.2	50.7
JUBLAT[e]	123.5	116.1	18.3	1.387	1.389	52.1	48.4
	123.4	115.8	−19.8	1.386	1.383	53.5	52.4
KAXXEM[f]	125.2	115.9	−8.6	1.389	1.381	56.1	52.7
MPATHB[g]	124.2	114.9	−9.9	1.395	1.386	53.9	57.4
PAMGEP[h]	124.2	115.2	−8.1	1.383	1.386	55.5	47.6
PAZMBU[i]	124.9	114.9	−2.1	1.392	1.389	51.3	52.5
PAZTBM[j]	123.3	115.9	0.8	1.383	1.376	53.1	52.5
PZACOX10[k]	122.8	116.2	19.7	1.382	1.382	52.8	50.0
	123.4	115.3	−0.7	1.377	1.366	56.3	57.4
SAGWEC[l]	124.3	115.7	−6.9	1.388	1.384	52.5	53.2
	124.5	115.6	6.0	1.386	1.380	53.7	54.6
1-Me-*p*-Br[13]	125.3	115.3	12.9	1.395	1.380	49.8	61.9
1,2-Me-*p*-Br[13]	125.4	115.4	1.0	1.387	1.379	57.8	56.2
1,2,3-Me-*p*-OMe[13]	123.2	116.3	8.8	1.386	1.386	52.7	50.0
1-Me-*p*-OMe[13]	125.4	116.3	−9.3	1.410	1.370	62.3	79.3
	125.1	116.1	−6.3	1.394	1.388	49.6	55.0
mean value	124.4	115.5	9.7	1.3872	1.3806	54.2	54.8

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Table 2. HF Calculated Bond Lengths C1C2 and C1C6 for 1,3,5-Tridiazobenzene of C_3 Symmetry with Various Fixed C−N=N Bond Angles (All Other Geometrical Parameters Being Optimized), the Resulting Kekule Structure Weights K_1, and the Total Energies

CNN angle (deg)	short CC bond C1C6 (Å)	long CC bond C1C2 (Å)	K_2 (%)	energy (hartree)
120	1.3762	1.3962	33.88	−557.227 993
116	1.3756	1.3972	33.48	−557.231 490
115.49	1.3756	1.3972	33.48	−557.231 540
112	1.3749	1.3978	32.40	−557.228 981
108	1.3740	1.3991	30.82	−557.219 178
104	1.3730	1.4010	28.75	−557.201 042
100	1.3721	1.4033	26.51	−557.173 546

zene, the latter being the strongest and imposing the direction of the bond fixation.

The main conclusion that may be drawn is that a benzene ring bearing open substituents may display an important bond fixation, one Kekule structure becoming twice as large as the other, provided the substituents are nonsymmetrical and unsaturated as in 1,3,5-tridiazobenzene. This is an extension of the original Mills−Nixon effect, formerly restricted to annelated aromatic rings. It is also of interest to note that little and very local perturbation of the π-electron structure of the ring is sufficient to break down the tendency of the ring to have C−C bonds of equal lengths. Instead, the trend to increase alternation is observed. These conclusions are strengthened by the theoretical calculations showing that the effect of localization of the π structure is enhanced by the subsequent addition of diazo groups in proper topology and conformation.

The origin of bond fixation in dazaobenzenes appears to be a blend of two driving forces that oppose each other: a minor angular strain effect that is more than compensated for by a major direct π electronic interaction tending to disfavor the Kekule structure displaying C=C and N=N bonds facing each other.

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