Analysis and Prediction of Angular Deformations in Phenyl Rings

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The geometry of the benzene ring is known to deviate from the ideal 6/*mmm* symmetry, when one (or more) of its hydrogen atoms is substituted.[1,2] Recently Domenicano, Vaciago and Coulson[3,4] have investigated the angular deformations in mono- and *para*-disubstituted benzenes in more detail. With the notations Δ_1, Δ_2, Δ_3 and Δ_4 for the deviations of the endocyclic bond angles from 120° at the *ipso*, *orto*, *meta* and *para* positions from the substituent, Domenicano *et al.* found that Δ_1 was linearly dependent on the electronegativity of the substituent and that the value of Δ_2 was approximately $-\Delta_1/2$. Furthermore, they concluded that Δ_3 and Δ_4 were scarcely if at all affected (*e.g.* $\Delta_3=\Delta_4=0$) and also that angular deformations induced by one substituent are usually unaffected by a second substituent *para* or *meta* to it.[5] However, in the case of substituents, like $-NH_2$, expected to interact with the π-system of the ring, Domenicano and Vaciago[6] have noted that a more complex pattern of distortions is obtained.

In order to interpret the statistically very significant angular deformations observed in recent accurate studies on multisubstituted benzene rings (*e.g.* Ref. 8), we found the earlier approaches inadequate. Thus, we have developed and tested a more general approach for the description and analysis of angular distortions.

Method. Let us make the following assumptions:

1. Additivity: The angular distortions in a highly substituted ring can be described as a superimposition of the effects from each substituent.

2. Symmetry: The distortion effect from each substituent has two-fold symmetry (two-fold axis through the *ipso* and *para* carbon atoms).

3. The distortions can be treated as independent of possible bond length effects caused by the substituents.

Provided that the ring can be considered planar, these assumptions imply that we need to specify three deformation parameters (*e.g.* Δ_1, Δ_2 and Δ_3) per substituent type since the fourth is given by the condition $\Delta_1+2\Delta_2+2\Delta_3+\Delta_4=0$. Thus, the distortion of an angle can be expressed as a linear combination of the effect from all the substituents.

With observations from several different related molecules a set of linear relations can be derived and solved by conventional least-squares techniques, using individual weights derived from the estimated variances of the angles.

The values of the different Δ's range from a few tenths of a degree up to a few degrees.[7] Thus, it would be advantageous to have observations of angular deformations with accuracies of about 0.2° or better, to test the validity of the present method.

Results. Preliminary deformation parameters for methyl and hydroxyl groups were determined from crystallographic data on five different structures, *viz.* 3,5-dihydroxytoluene,[8] 2,5-dihydroxytoluene,[8] durene,[9] resorcinol[10] and catechol.[11] The experimental data are listed in Table 1. From the altogether 27 observations, the following 6 independent parameters were obtained as the weighted least-squares solution (°):

	Δ_1	Δ_2	Δ_3	(Δ_4)
CH_3-	−1.9(1)	1.0(1)	0.3(1)	−0.7(1)
HO−	0.5(1)	−0.5(1)	0.5(1)	−0.5(1)

Obviously, the distortion effects from methyl are such that $\Delta_2 \approx -\Delta_1/2$, in accordance with the earlier suggestions by Domenicano *et al.*[3] However, the distortion −0.7(1) at the *para* position deviates significantly from 0°. The effects from a hydroxy-group are completely different by yielding a constant but alternating deformation of 0.5° over the whole benzene ring. This difference is probably due to the fact that the hydroxy-group, but not the methyl, is a strong π donor (see, *e.g.*, Refs. 13 and 14).

To test whether the weighted differences between

Table 1. Observed deviations (°) from 120° by the endocyclic bond angles for the five methyl- and hydroxy-substituted benzenes used in the present study.

Compound	Ref.	C-1	C-2	C-3	C-4	C-5	C-6
1-Methyl-2,5-dihydroxybenzene	8	−1.96(15)	1.25(15)	0.01(17)	−0.99(16)	0.69(15)	0.98(16)
1-Methyl-3,5-dihydroxybenzene	8	−0.41(12)	−0.22(11)	1.03(11)	−1.39(11)	1.17(10)	−0.17(12)
1,2,4,5-Tetramethylbenzene	9	−1.44(11)	−1.41(11)	2.86(14)			
1,3-Dihydroxybenzene	10	1.28(20)	−1.08(28)	0.93(20)	−0.98(22)	0.90(29)	−1.06(26)
1,2-Dihydroxybenzene	11	0.14(17)	−0.19(20)	0.07(20)	0.11(17)	−0.25(15)	0.11(15)

the bond angle observations and the least-squares estimates have a normal distribution, a half-normal probability plot[15] was performed. The linearity (correlation coefficient 0.988) of this plot indicates that a normal distribution of differences is not unreasonable. The slope suggests that the e.s.d.'s of either the observed or calculated values are slightly underestimated by a factor of 1.1. A plot of observed *versus* calculated bond angle distortion yields a correlation coefficient of 0.978. The root mean square (r.m.s.) deviation between observed and calculated values was 0.21°.

As another check on the validity of this method of treating angular distortions, a different combination of substituents, *viz.* chloro- and phenyl-substituents have been analyzed. The experimental data used consist of the preliminary but fairly accurate crystal structure determinations[12] of three chloro-substituted biphenyls (2,5,2′,6′-tetra-, 2,5,2′,5′-tetra- and 2,3,4-trichlorobiphenyl). The 6 distortion parameters for chloro- and phenyl-substituents given below were thus determined from 30 observations with e.s.d.'s of 0.2° (°):

	Δ_1	Δ_2	Δ_3	(Δ_4)
Chloro-	1.0(1)	−1.1(1)	0.7(1)	−0.4(1)
Phenyl-	−2.0(1)	0.8(1)	0.5(1)	−0.6(1)

In this case the correlation coefficient for the halfnormal probability plot (slope 1.2) is 0.993 and that for the plot of observed *versus* calculated angle distortions is 0.982. The r.m.s. deviation is 0.29°. According to our results the phenyl distortions were found to be independent of the biphenyl conformation. The distortion effects from the π-donating chloro-substituent show a similar alternating pattern as was obtained for the π-donating hydroxy-substituent. The similarity between the values obtained for the phenyl- and the methyl-groups is very close.

In the analysis of chloro-substituted biphenyls, two sets of data, *viz.* those of 2,4,5,2′,4′,5′-hexachlorobiphenyl[16] and of biphenyl[17] itself were left out of the least-squares determination of the Δ's. Both these structural investigations have yielded e.s.d.'s in the bond angles of about 0.2°. These observations can thus be utilized to illustrate the possibility of reliable predictions of endocyclic bond angles. The bond angles (°) for biphenyl are averaged.

	C-1	C-2	C-3	C-4	C-5	C-6
Hexachlorobiphenyl						
Obs.	117.6	121.8	119.7	119.7	120.0	121.2
Calc.	117.3	122.1	119.2	120.1	120.1	121.2
Biphenyl						
Obs.	117.9	120.9	120.7	118.9		
Calc.	118.0	120.8	120.5	119.4		

In conclusion, the outcome of our analysis indicated that the endocyclic angular distortions of also very highly substituted benzene derivatives can be predicted with an accuracy of about 0.2° by determining three deformation parameters per substituent type. This accuracy is of the same order as that obtained in accurate crystal structural investigations by diffraction methods.

The investigations described here are presently being extended to several other types of substituted phenyl rings. Studies of these effects by molecular orbital calculations are in progress.

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