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The Imbalanced Kekule Structure Contributions in the Ring in 1,3,5-trisubstituted Benzene Derivatives: Low Temperature X-Ray Study on 1,3,5-trimethoxybenzene, and *ab initio* Calculations on 1,3,5-triformylo - benzene and trimethoxy-benzene and the Related Di-substituted Systems.

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Abstract. A low temperature X-ray structural determination for 1,3,5-trimethoxybenzene reveals π-electron localisation in the ring. *ab initio* calculations for 1,3,5-trimethoxybenzene and 1,3,5-triformylobenzene show that these nonsymmetrical substituents induce opposite imbalance of Kekule structures in the ring. An empirical rule is proposed - that *cis* CC-bonds in the ring show increased double bond character (compared to the *trans* bond) when the substituent is of X-Y kind (with a single XY bond), and less double bond character if the substituent is of the X=Y type (with a double XY bond). Additional calculations for *cis* and *trans* conformers of 1,4-dimethoxybenzene differ dramatically in the degree of π-electron localisation, supporting the idea that the dominating factor of these distortion is a through-space effect. Copyright © 1996 Published by Elsevier Science Ltd

Introduction

The shape of the benzene ring, its deformations and the roles of σ - and π - electrons in these problems have been intensively studied in the last decade. An accurate, low temperature neutron diffraction study of crystalline benzene showed that the ring is folded (chair conformation)[1]. Shaik, Hiberty and co-workers argued in a series of papers[2-4] that the D_{6h} structure of benzene ring is due to the tendency of the σ-electron skeleton to retain unchanged bond lengths, whereas π-electrons tend to be localised (alternation of bond lengths) leading to the D_{3h} structure. The same conclusion was reached in an independent way by Jug and Koester[5]. Thus aromatic character is said to be (at least partly) a by-product of the σ-electron constraint on the molecular geometry.

The decisive role of the σ-electron structure in stabilisation of the benzene ring has very recently been questioned[6]. However, recent studies of the aromatic character of chrysene and its EDA-complexes with fluoranil and TCNQ revealed that pumping out π-electrons from the chrysene moiety increases its aromatic character[7]. Alternation of bond lengths in central rings considerably decreases in chrysene molecules involved in

EDA complexes, in comparison to those of the „free" molecule[8]. This appeared to be the first experimental evidence supporting the idea of Shaik and Hiberty.

Recently it was also shown that deformations of HCC bond angles from 120° to 90° leads to significant deformations of the ring geometry, which may be represented by unequivalent weights of the Kekule structures[9] i.e. D_{3h} symmetry of the ring. In the recent monograph on aromaticity[10] the problem D_{3h} symmetry of benzene is reviewed, where only the detection of small effects is problematic.

We noted in our recent *ab initio* study of anisole[11] that the MeO group induces unequal amounts of the Kekule structure of the ring (Fig. 1) with shortening of the ipso-ortho CC-bond *cis* to the O-Me bond of the methoxy group. The effect of alternation is propagated around the whole ring, i.e. it is not a local effect. Estimates of the relative weights of these Kekule structures using the HOSE model[12] yielded the ratio 52.6 : 47.4.

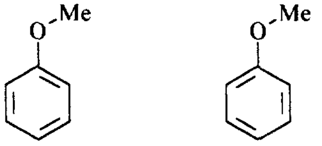


Fig. 1.Kekule structures and their relative weights for anisole.

To support this theoretical finding we have looked for experimental evidence. In the case of sym-trimethoxybenzene, the published X-ray crystal structure at room temperature[13] and at 203K[14] appear to show an enhanced D_{3h} - type deformation in the ring. However the support is only qualitative due to too low precision of the measurements.

Results and Discussion

Since this molecule appears to provide tantalizing evidence for the reality of our observation in the computer experiment, we have carried out a more precise low temperature X-ray crystal structure determination of 1, 3, 5-trimethoxybenzene. In order to obtain a deeper understanding of these substituent effects we have also undertaken Hartree-Fock (HF) geometry optimisations for various conformers of the free molecule, including a determination of the barrier for rotation of one methoxy group.

The X-ray crystal structure determination at 115K utilised equipment and techniques which have been described previously.[15] Refinement on the 2376 unique reflections with $F_o > 4\sigma(F_o)$ using SHELX-93[16] yielded an R-value (based on F) of 0.0347 and goodness - of - fit = 1.046. The full details of this structure determination will be published as a part of a statistical study of many such structures[17].

The HF calculations employed GAMESS[18] running on an Alpha Risc 3000 work station, using the Direct SCF scheme as implemented in the package. The tolerance for optimisations taken as 2×10^{-4} a.u.(maximum force on a nucleus) and 1×10^{-4} (RMS force). Optimisations employed the 6-31G* basis set[19] and single -point 6-311G**[20] calculations were undertaken at the optimised geometries (6-311G**//6-31G*) to obtain improved estimates of the electronic energy differences. The optimisations included: the C_{3h} form (see Fig. 2, $\chi = 0°$); four constrained optimisations (with no symmetry) in which χ was fixed at 45 °, 90 °, 135 ° and

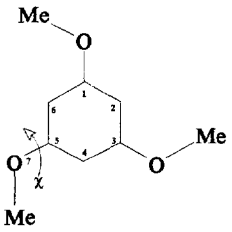


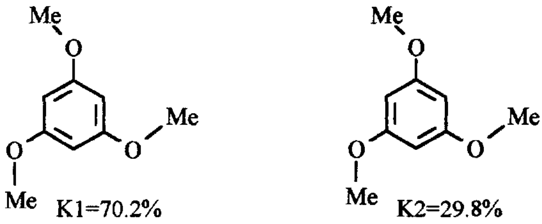
Fig. 2.Conformational scheme for 1,3,5-trimethoxybenzene.

180 ° respectively, with all other geometrical parameters optimised; and a C_{3v} form in which all 3 methoxy groups are perpendicular to the ring (all *cis* to each other).

Table 1. Ring bond lengths (in A) of 1,3,5-trimethoxybenzene. (HF/6-31G* optimised and experimental), and computed weights of Kekule structures, K1 and K2 (Fig. 3).

Bond\\χ(A°)	0	45	90	135	180	all 90	Exp.(esd) ($\chi\cong 180^\circ$)
C1-C2	1.4015	1.3984	1.3975	1.3954	1.3915	1.3851	1.397(1)
C2-C3	1.3754	1.3784	1.3799	1.3811	1.3819	1.3851	1.390(1)
C3-C4	1.4015	1.3983	1.3977	1.3954	1.3908	1.3851	1.395(1)
C4-C5	1.3754	1.3751	1.3723	1.3742	1.3767	1.3851	1.388(1)
C5-C6	1.4015	1.3967	1.3952	1.3977	1.4061	1.3851	1.399(1)
C6-C1	1.3754	1.3792	1.3809	1.3821	1.3841	1.3851	1.390(1)
C5-O2	1.3448	1.3530	1.3611	1.3541	1.3510	1.3609	1.368(1)
K1	70.2%	65.8%	64.9%	63.4%	62.0%	50.0%	56.4%
K2	29.8%	34.2%	35.1%	36.6%	38.0%	50.0%	43.6%

The high-precision geometry of 1,3,5-trimethoxybenzene, (Table 1, column 8) verifies the hypothesis of unequal Kekule structure weights of the ring. Application of the HOSE model[12] to the experimental bond lengths yields the ratio 56.4:43.6, indicating significant alternation of the π-electron structure (for definition of Kekule structure cf. Fig. 3).



K1=70.2% K2=29.8%

Fig. 3. Scheme of Kekule structures and their weights for 1,3,5-trimethoxybenzene

In the crystalline state 1,3,5-trimethoxybenzene does not exhibit C_{3h} -type symmetry, since one methoxy group is twisted with χ nearly 180 ° (see Fig. 2). The calculated total energies (Table 2) indicate that this is not the referred conformation for the free molecule, since the C_{3h} conformation (Table 1) has an energy some 9 kJ/mole lower that the χ = 180° conformation (Table 2). This is possibly a shortcoming of the calculations, since it was impossible to compute zero point energy corrections with such large basis sets, but it is more likely that, in the crystal the molecules can simply pack more efficiently in this lower symmetry conformation. The χ = 180° calculated conformation shows the same D_{3h} - type deformation of the ring observed experimentally, only more pronounced (relative Kekule structure weights 62.0:38.0). The lowest energy (C_{3h}) conformation, in which the three methoxy groups cooperatively act on the π electron structure of the ring, shows even more pronounced alternation of bond lengths, with relative weights of Kekule structure 70.2:29.8. As one methoxy group is rotated the relative Kekule structure weights change monotonically (see the lowest lines in Table 1). Energetically all conformers based on one methoxy group rotating are not too strongly separated - they all occur within 12 kJ/mole of the global minimum (C_{3h} type structure). If all three methoxy groups are forced to be perpendicular to the ring plane, the total energy increases by roughly three times the amount found with just one group perpendicular (see Table 2).

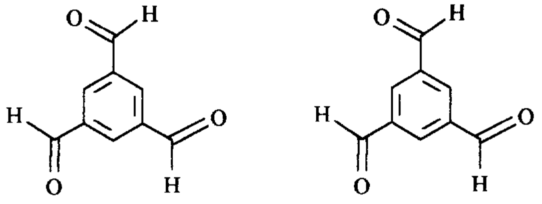
Table 2. Total energies of 1,3,5-trimethoxy benzene and its conformers

χ (°)	6-31G*//6-31G* (kJ/mole)	6-311G**//6-31G* (kJ/mole)
0	0[a)]	0[b)]
45	8.2	8.3
90	11.5	11.9
135	11.5	12.0
180	6.1	9.3

a) relative to E= - 572.34822 Hartrees
b) relative to E= - 572.48778 Hartrees

With all three groups perpendicular (and *cis* to each other) E(HF/6-31G*) = -572.33630 Hartrees or 31.1 kJ/mole higher than the C_{3h} coplanar conformation. If this localisation effect of the methoxy substituent were due to a combination of resonance and inductive effects, that is to say through bond only, then the ring geometry for χ = 0° and χ = 180° should be identical. However the data in Table 1 show that this is not the case, and therefore through - space interactions must play a significant (possibly dominant) role.

In order to explore the nature of the substituent effect further, we have also carried out a 6-31G* optimisation of 1,3,5 - triformyl benzene. The formyl group is a typical electron-withdrawing group (Hammett meta and para substituent constants are 0.36 and 0.43, respectively[21]), by comparison with the methoxy group (0.12 and -0.27[21], respectively). The resulting ring bond lengths alternate between 1.397 A (*cis* to the C=O bond) and 1.379 A (*trans*), with associated Kekule structure imbalance K1 = 35.8% and K2=64.2% (Fig. 4). Evidently, both withdrawing and donating substituents can cause this localisation effect, but in opposite directions



K1=35.8% K2=64.2%

Fig. 4. Scheme of the Kekule structure weights for 1,3,5-triformylobenzene.

To strengthen the hypothesis of the through space nature of the interaction of the non-cylindrical substituents on the π electron structure of the benzene ring we have additionally carried out 6-31G* calculations for two conformers, *cis* and *trans*, of 1,4 - di - methoxy - and 1,4 - di-formylo - benzene. The resulted Kekule structure weights are given in Fig. 5.

K1=67.4% K1=50.0%

Fig. 5. Kekule structure weights for cis and trans conformers of 1,4-dimethoxybenzene

Clearly there is strong CC bond alternation in the *cis* conformer, but this is negligible in the *trans* conformer, despite the fact that both conformers have identical through bond substituent effects. Looking at the results presented in Figs 1 through 5 an approximate phenomenological rule may be deduced: the non-cylindrical XY substituent with a single XY bond induces more double C1C2 bond and less double C6C1 in the ring. If the XY has a double X=Y bond then the C1C2 bond become less double than the C6C1. It should be mentioned also that in experimental geometry of symmetric triethyl derivatives of boraxin, borazine and triazine a similar effect as observed for sym trimethoxybenzene has been recently observed[14]. The same effect has also been found experimentally for 2,4,6-trimethoxy-*s*-triazine[22] and diazoderivatives of benzene[23].

In conclusion: it may be said that subtle mostly through-space interactions between the methoxy (or formyl) groups and the π-electron structure of the benzene ring lead to significant bond length alternation which is equivalent to the decrease of aromatic character of the ring[24,25]. These effects are maximal in the 1,3,5-trisubstituted species, and hence are observed even in the crystalline state (where other effects can operate to confuse the picture). The largest effect is in the C_{3h} conformer which is not accessible experimentally (at least in the solid state), but this is shown by the *ab initio* calculations presented here. We suggest that these results may be interpreted as supporting the Shaik-Hiberty hypothesis, which invokes finely-balanced σ and π contributions in determining the benzene ring geometry with a slight domination of σ stabilisation (favouring equal bond lengths in the ring). An additional important finding is that the direction of the localisation for electron withdrawing substituents is opposite to that for electron donating substituents. We should emphasise that nonsymmetrical substituents like the methoxy or formyl groups which induce unequal contributions of the Kekule structures must modify the chemical and physicochemical properties of the ring. Moreover, since these kind of substituents undergo thermal oscillations (in - and out- of plane), with amplitudes of up to 5°[26] at ambient temperatures, the actual degree of π localisation is also in a state of oscillation (assuming the Born - Oppenheimer approximation) which may lead to additional, perhaps unexpected, effects.

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