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Commentationes

Localized Molecular Orbitals for Aromatic Molecules

Mono- and Disubstituted Benzenes

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Localized molecular orbitals are calculated using the method of Boys for the aromatic molecules C_6H_6, C_6H_5X and the *p*-, *m*-, and *o*-forms of C_6H_4XY, where X,Y = CN,OH,F. The calculations are performed both with and without the constraint of σ, π-separation in the localization. The localized π-orbitals are multicenter bonds. If the σ- and π-orbitals are localized together, two different structures are found, Kekulé-type structures and structures with a set of six two center and a set of three three center bonds. The C–X bond turns out to be a single bond if X = CN and a double bond, if X = OH or F.

Key words: Aromatic molecules – Benzenes, mono- and disubstituted ~ – C_6H_4XY, para-, meta-, and ortho-forms of ~ – Localized molecular orbitals

1. Introduction

In the description of molecules by wave functions localized molecular orbitals (LMO's) correspond to the classical chemical concepts of inner shells, lone pairs of electrons, and bonds. They have first been introduced by Hund [1] and by Lennard-Jones and coworkers [2]. The interest in LMO's has increased after the work of Edmiston and Ruedenberg [3] and Boys [4] and has led to the development of a number of localization methods both intrinsic and external [5] in character [3, 4, 6–8]. A recent review has been given by Weinstein, Pauncz, and Cohen [9]. There exists a number of articles applying in particular the localization method of Edmiston and Ruedenberg [3] to diatomic and polyatomic molecules [10–19]. (The references should indicate some main trends, but are not assumed to be complete.) Few investigations, however, deal with the localization of molecular orbitals (MO's) in aromatic molecules, where the orbitals are usually regarded as delocalized in the molecular orbital theory [14, 20–22]. The LMO's calculated by Newton and Switkes for benzene are to the knowledge of the author the only LMO's obtained from an *ab initio* wave function by the intrinsic Edmiston-Ruedenberg localization method [14]. Other articles invoke the INDO approximation [20] or investigate only the π-orbitals in the Hückel-Wheland approximation [21, 22]. In the present article LMO's are reported for a number of mono- and disubstituted benzene derivatives (C_6H_6, C_6H_5X, and *p*-, *m*-, *o*-C_6H_4XY, where X, Y = CN, OH, F) calculated from *ab initio* wave functions for these molecules. External localization methods such as the one of Magnasco and Perico [8] did not appear appropriate because they require a concept of the structure of the LMO's prior to the localization. Unprejudiced results can only be obtained by an intrinsic method. The localization method of Boys [4] was chosen because it requires the least computational expense from among the intrinsic methods. The method of Edmiston and Ruedenberg, which is based on the minimization of the Coulomb and exchange energies between different orbitals, may be physically more appealing than the method of Boys, in which the sum of the separations of the orbital charge centroids is maximized, but it was found that in many cases the results of the two methods are in excellent agreement with each other [19]. In the subsequent section the wave functions calculated for the benzene derivatives will be shortly described and the LMO's discussed.

2. Calculations

The molecules considered in this work are besides C_6H_6 itself of the type C_6H_5X, and C_6H_4XY, where X and Y can be CN, OH, and F. All the disubstituted benzenes are examined in their *p*-, *m*-, and *o*-forms. The geometries used in the calculations are partly taken from the literature [23] partly idealized geometries have been used. The geometry of the benzene molecule has been used in all the substituted products. The bond distances of the CN, OH, and F substituents are taken from the monosubstituted compounds and have been used also in the disubstituted molecules: (CN : $R(CC) = 1.419$ Å, $R(CN) = 1.158$ Å; OH : $R(CO) = 1.36$ Å, $R(OH) = 0.956$ Å, $\sphericalangle COH = 120°$; F : $R(CF) = 1.30$ Å). The COH angle was chosen to be 120° with all atoms lying in a plane. In the *p*-dihydroxybenzene the two H atoms of the OH groups are in cisposition, i.e. the molecule has only planes of symmetry but no inversion center. The *m*- and *o*-dihydroxybenzenes are derived from this structure by rotating one of the OH groups (the group on C atom C_4) counterclockwise into these positions. (The standard numbering system for the C atoms in the benzene ring is used, the H atoms carry the same indices as the C atoms to which they are bound.) In this way no intramolecular hydrogen bonds can be formed in the *o*-compound and the H atoms of the OH groups have the least sterical interaction. The same geometries for the OH groups have been used in the compounds C_6H_4CNOH and C_6H_4OHF. All bond distances and angles were kept fixed in the calculations.

The basis set used for the computation of the wave functions is a minimal atomic Gaussian lobe function basis, whose parameters are taken from the literature [24, 25]. The contraction coefficients were determined from calculations on small molecules. On the atoms C, N, O, and F 3 functions of *s*-type [24] contracted to two functions and one function of *p*-type [24] and on the H atoms one function of *s*-type has been used [25]. (The basis set has been given in Ref. [26].) It is certainly of poor quality, but since a qualitative information about the structure of the LMO's is desired, it should suffice for the purpose. The total SCF energies computed for all compounds are listed in Table 1. It is to be noted that the *m*-disubstituted benzenes are always the most stable compounds in the cases considered and the *o*-disubstituted compounds are always the least stable ones having the highest total energies. The results of these calculations are discussed in more detail elsewhere [26].

Table 1. Total SCF energies for C_6H_6. C_6H_5X, and the *p*-, *m*-, and *o*-forms of the disubstituted benzenes C_6H_4XY with X,Y = CN,OH,F. (All values in atomic units)

Molecule	E,E(para)	E(meta)	E(ortho)
C_6H_6	-218.787381		
C_6H_5CN	-305.560816		
C_6H_5OH	-289.044239		
C_6H_5F	-311.120131		
$C_6H_4(CN)_2$	-392.334033	-392.334281	-392.332991
C_6H_4CNOH	-375.817025	-375.817745	-375.813919
C_6H_4CNF	-397.892863	-397.893164	-397.891027
$C_6H_4(OH)_2$	-359.285606	-359.302633	-359.273415
C_6H_4OHF	-381.358415	-381.378588	-381.341240
$C_6H_4F_2$	-403.430215	-403.454093	-403.394930

The MO's of the wave functions of these molecules have been localized using the method of Boys [4] in two different ways. In the first calculation (A) the MO's of σ- and π-symmetry have been localized separately. This serves in particular to investigate the structure of the localized π-orbitals, which are usually regarded as delocalized. In the second calculation (B) the MO's of different symmetry are localized together. Previous calculations of LMO's in systems containing σ- and π-orbitals by intrinsic localization methods have led to the conclusion that a σ, π-separation is a saddle point solution in the localization process and better localized orbitals are obtained, if the orbitals of different symmetry are allowed to mix [10, 11, 13, 14, 19]. This has been found also for benzene [14]. In the present article this question will be examined too. It will be seen that the calculation B always gives better localized orbitals, although it has not been examined whether a unique maximum is occurring.

To avoid duplicating statements about the LMO's in the different molecules some general remarks will be made here. If the σ- and π-type MO's are localized separately, the CH and CC σ-type LMO's have the expected features. If a CN group is present, it is characterized by two diagonally equivalent CN bond LMO's and a π-type bond orbital. The latter is always more polarized towards the benzene ring, whereas the digonal LMO's have their charge centroids nearly in the middle of the bond. It seems that the benzene ring "attracts" the π-orbital, although there is no indication of a C_1–C double bond. In addition the N atom has a σ-type lone pair LMO, which is nearly unaffected by the character of further substituents on the benzene ring. If an OH group is present, it is linked to the C atom of the ring by two bond orbitals, whose structure will be discussed below. The other LMO's are a σ-type OH bond orbital and a σ-type lone pair LMO. The substituent F behaves very similarly, only the OH bond LMO is replaced by a second lone pair orbital.

Calculation B leads always to a mixture of the MO's of σ- and π-symmetry; the CH bond orbitals remain nearly unchanged compared to the case above, the

CC bond LMO's, however, show different structures. Kekulé-type structures are found as well as a set of two center and another set of three center bond orbitals plus intermediate structures showing a considerable distortion. The details will be discussed below. The appearance of distorted and nonequivalent LMO's can be due to the fact that a number of structures having approximately the same degree of localization exist. The maximum of the separation of the orbital charge centroids is then determined on a rather flat surface. The bond orbitals of the CN group are expected to mix and give trigonal banana bond orbitals, which is found to be the case. The N lone pair and the OH bond orbital remain essentially unaffected, whereas the lone pair orbitals (on the O and F atom) experience a small distortion, which is not believed to be significant. In the calculations to be described below the subsequent points will be considered. In calculation A the structure of the orbitals linking the C atom of the ring to a substituent and the structure of the π-orbitals, in calculation B the structure of the orbitals which represent the bonds to the substituents and the structure of the CC bond orbitals will be discussed.

For the molecules representing typical cases a table is given containing the charge centroids of the LMO's as information on their structure. The inner shell MO's have in all cases been included in the localization process, but their charge centroids are omitted from the tables to save space, because they are of little concern to the present investigation. But there remains still too much information. The following procedure was thus adopted. The complete tables will only be given for benzene itself and the monosubstituted products. From these tables some information can be derived, which influence the substituents have on the structure of the LMO's in inducing a charge rearrangement. For the disubstituted benzene molecules the tables will contain the following information, which is considered to be of the greatest interest in the present context. For calculation A the charge centroids will be given for the CX bond orbitals and for the localized π-orbitals, for calculation B the charge centroids will be given for the CX and for the CC bond orbitals.

In describing the LMO's the notation introduced by Edmiston and Ruedenberg [10] and England and Ruedenberg [21, 22] (for the localized π-orbitals) will be used. In the molecules under investigation only the orbitals of type $\pi l2$ (essentially a two center bond orbital with intermediate contributions from the two neighbouring C atoms and smaller ones from the remaining C atoms of the benzene ring), of type $\pi l3$ (essentially a three center LMO with a smaller contribution from the C atom farthest away), and the intermediate types denoted by England *et al.* by $\pi l23$, which can be either closer to a $\pi l2$- or a $\pi l3$-type orbital, can occur. The distorted orbitals mentioned above, which are always found to be mixtures of σ- and π-orbitals, cannot in many cases be described in the notation commonly employed [10, 21, 22]. Where this standard notation does not apply the following notation will be used: $biABC\ldots$, where b denotes a bond orbital (only this case will be needed), i the number index of the orbital, if there is more than one between the atoms, and $A, B, C, \ldots$ are the centers which contribute most strongly to the charge density associated with the particular LMO. It should be noted that for the aromatic molecules considered here it is in some cases somewhat arbitrary whether a given bond LMO should be called a two

Table 2. Charge centroids of the LMO's of C_6H_6

A: σ, π			B: $\sigma + \pi$			
LMO	X	Y	LMO	X	Y	Z
$b\sigma c_1H_1$	0.0	4.075	$b\sigma c_1H_1$	0.0	4.073	0.0
$b\sigma c_2H_2$	3.529	2.037	$b\sigma c_2H_2$	3.527	2.036	0.0
$b\sigma c_3H_3$	3.529	-2.037	$b\sigma c_3H_3$	3.527	-2.036	0.0
$b\sigma c_4H_4$	0.0	-4.075	$b\sigma c_4H_4$	0.0	-4.073	0.0
$b\sigma c_5H_5$	-3.529	-2.037	$b\sigma c_5H_5$	-3.527	-2.036	0.0
$b\sigma c_6H_6$	-3.529	2.037	$b\sigma c_6H_6$	-3.527	2.036	0.0
$b\sigma c_1c_2$	1.147	1.987	$b\sigma c_2c_3$	2.324	0.0	0.0
$b\sigma c_2c_3$	2.294	0.0	$b\sigma c_4c_5$	-1.162	-2.013	0.0
$b\sigma c_3c_4$	1.147	-1.987	$b\sigma c_6c_1$	-1.162	2.013	0.0
$b\sigma c_4c_5$	-1.147	-1.987	$bd1c_1c_2$	1.007	1.744	0.463
$b\sigma c_5c_6$	-2.294	0.0	$bd2c_1c_2$	1.007	1.744	-0.463
$b\sigma c_6c_1$	-1.147	1.987	$bd1c_3c_4$	1.007	-1.744	0.463
$\pi\ell 23c_1c_2c_3$	1.316	1.174	$bd2c_3c_4$	1.007	-1.744	-0.463
$\pi\ell 23c_3c_4c_5$	0.359	-1.727	$bd1c_5c_6$	-2.014	0.0	0.463
$\pi\ell 23c_5c_6c_1$	-1.675	0.552	$bd2c_5c_6$	-2.014	0.0	-0.463

center or a three center bond orbital. The coordinate system used in the subsequent Tables 2–10 has its origin at the center of the benzene ring, the molecules lying in the x, y-plane with the atoms C_1 and X on the positive y-axis. Atomic units have been used throughout.

C_6H_6 (Table 2)

Calculation *A* leads to the expected σ-type bond orbitals between neighbouring C and H atoms and to three bonding orbitals of type $\pi l 23$ (Table 2, the z-component of the charge centroids is not given because it is identically equal to zero). They are three center bond orbitals, whose charge density extends appreciably over three centers. A nodal surface passes through the two neighbouring C atoms (or very close to them) and some charge density resides on the remaining C atom. As pointed out [10] there exists a "continuous infinity of sets of equally localized equivalent orbitals", which can be of the symmetric type $\pi l 2$ or $\pi l 3$ or any structure intermediate between the two. The structure which has been obtained in this work is close to $\pi l 3$. No attempt was made to obtain the completely symmetric structure or any of the other ones because this has already been done [21]. If the σ- and π-orbitals are jointly localized (*B*) there does no longer exist this infinity of structures. Localization should give either of the two Kekulé-type structures, which has been observed before [14, 20] and is found in the present investigation as well (Table 2).

Table 3. Charge centroids of the LMO's of C_6H_5CN

A: σ, π			B: $\sigma + \pi$			
LMO	X	Y	LMO	X	Y	Z
bd1CN	0.543	6.391	bt1CN	-0.498	6.370	-0.144
bd2CN	-0.543	6.391	bt2CN	0.379	6.339	-0.345
$b\sigma C_1C$	0.0	3.905	bt3CN	0.118	6.299	0.489
$\ell\sigma N$	0.0	8.084	$b\sigma C_1C$	-0.001	3.904	-0.001
$b\sigma C_2H_2$	3.534	2.042	$\ell\sigma N$	0.0	8.082	0.0
$b\sigma C_3H_3$	3.531	-2.039	$b\sigma C_2H_2$	3.532	2.041	0.0
$b\sigma C_4H_4$	0.0	-4.078	$b\sigma C_3H_3$	3.529	-2.038	0.0
$b\sigma C_5H_5$	-3.531	-2.039	$b\sigma C_4H_4$	0.0	-4.076	0.0
$b\sigma C_6H_6$	-3.534	2.042	$b\sigma C_5H_5$	-3.529	-2.038	0.0
$b\sigma C_1C_2$	1.141	1.998	$b\sigma C_6H_6$	-3.532	2.041	0.0
$b\sigma C_2C_3$	2.297	-0.005	$b\sigma C_1C_2$	1.156	2.026	0.0
$b\sigma C_3C_4$	1.148	-1.987	$b\sigma C_3C_4$	1.163	-2.013	0.0
$b\sigma C_4C_5$	-1.148	-1.987	$b\sigma C_5C_6$	-2.326	-0.006	0.0
$b\sigma C_5C_6$	-2.297	-0.005	$bd1C_2C_3$	2.017	0.001	0.465
$b\sigma C_6C_1$	-1.141	1.998	$bd2C_2C_3$	2.017	0.001	-0.465
$b\pi CN$	0.0	6.226	$bd1C_4C_5$	-1.011	-1.737	0.463
$\pi\ell 3C_2C_3C_4$	1.528	-0.871	$bd2C_4C_5$	-1.011	-1.737	-0.463
$\pi\ell 3C_4C_5C_6$	-1.526	-0.874	$bd1C_6C_1$	-1.001	1.773	0.458
$\pi\ell 3C_6C_1C_2$	-0.002	1.813	$bd2C_6C_1$	-1.001	1.773	-0.458

C_6H_5CN, C_6H_5OH, C_6H_5F (Tables 3–5)

The π-type LMO's of C_6H_5CN (Table 3) separate into two distinct subsets: a CN π-orbital which has very little contribution from the $2p$ π-type functions on the other C atoms and is thus well localized, and a set of three orbitals in the benzene ring of type $\pi l3$, which are much less localized. This is in contrast to the results for C_6H_5OH (Table 4) and C_6H_5F (Table 5). In these two molecules the π-orbitals cannot be separated into sets localized with respect to each other. One of the π-orbitals is always a C_1X π-type LMO, which is polarized towards the atom X but still has a strong delocalization onto the neighbouring C atoms of the benzene ring (C_2 and C_6). The other π-orbitals are localized in the ring and are of type $\pi l23$ and $\pi l3$, respectively, for the bond $C_3C_4C_5$ (Table 4, 5). The substituents OH and F (which are in electrophilic substitutions on the benzene ring p- and o-directors) thus show a remarkable difference from the substituent CN. The structure of C_6H_5OH and C_6H_5 F as indicated by the structure of the LMO's in this calculation is thus closer to the mesomeric forms $^{\ominus}C_6H_5OH^{\oplus}$ and $^{\ominus}C_6H_5F^{\oplus}$ with C_1–O and C_1–F double bonds than to the

Table 4. Charge centroids of the LMO's of C_6H_5OH

A: σ, π			B: $\sigma+\pi$			
LMO	X	Y	LMO	X	Y	Z
$b\sigma C_1O$	-0.048	4.063	$bd1C_1O$	-0.017	4.397	-0.391
$b\sigma OH$	-0.996	5.764	$bd2C_1O$	-0.010	4.449	0.398
$\ell\sigma O$	0.405	5.355	$b\sigma OH$	-0.989	5.767	-0.001
$b\sigma C_2H_2$	3.534	2.050	$\ell\sigma O$	0.378	5.360	-0.005
$b\sigma C_3H_3$	3.535	-2.037	$b\sigma C_2H_2$	3.534	2.050	0.0
$b\sigma C_4H_4$	0.0	-4.088	$b\sigma C_3H_3$	3.534	-2.037	-0.001
$b\sigma C_5H_5$	-3.536	-2.042	$b\sigma C_4H_4$	0.0	-4.088	0.001
$b\sigma C_6H_6$	-3.542	2.063	$b\sigma C_5H_5$	-3.535	-2.042	-0.001
$b\sigma C_1C_2$	1.152	2.028	$b\sigma C_6H_6$	-3.541	2.062	0.0
$b\sigma C_2C_3$	2.285	-0.001	bC_1C_2	1.156	2.025	-0.060
$b\sigma C_3C_4$	1.155	-1.984	bC_2C_3	2.265	0.034	-0.203
$b\sigma C_4C_5$	-1.153	-1.983	bC_3C_4	1.150	-1.987	-0.090
$b\sigma C_5C_6$	-2.297	-0.003	bC_4C_5	-1.147	-1.985	-0.090
$b\sigma C_6C_1$	-1.181	1.986	bC_5C_6	-2.284	0.022	-0.171
$b\pi C_1O$	0.0	4.790	bC_6C_1	-1.185	1.983	-0.064
$\pi\ell 23C_1C_2C_3$	1.742	0.816	$bC_1C_2C_3$	1.764	0.769	0.263
$\pi\ell 3C_3C_4C_5$	0.006	-1.862	$bC_3C_4C_5$	-0.003	-1.846	0.180
$\pi\ell 23C_5C_6C_1$	-1.738	0.811	$bC_5C_6C_1$	-1.744	0.792	0.235

structures involving only a single bond. (Note: in the above formulas it would be better to write a $\delta\pm$ because of the polarity of the CX bond orbitals.) The O atom consequently has only a single and the F atom two digonally equivalent lone pair LMO's.

In calculation *B* the C_1X bond LMO remains a single bond LMO if X is CN, in the other cases two equivalent bond LMO's result. The lone pair LMO's remain the same as described above. For the CC bond LMO's in the ring one obtains a Kekulé-type structure for the cyano-compound (Table 3) with three single and six banana bond orbitals. For C_6H_5OH and C_6H_5F six CC two center and three center bond LMO's are found. All these CC bond LMO's cannot be classified as σ or π, but are mixtures which show a distortion from equivalent orbitals. No attempt was made to transform these into equivalent orbitals which certainly should be possible.

p-, *m*-, *o*-$C_6H_4(CN)_2$

The LMO's calculated for *p*-, *m*-, and *o*-$C_6H_4(CN)_2$ are very similar to the LMO's of C_6H_5CN. In calculation *A* the π-orbitals separate again into several sets which appear to be well localized with respect to each other, a π-orbital in

Table 5. Charge centroids of the LMO's of C_6H_5F

A: σ, π			B: $\sigma + \pi$			
LMO	X	Y	LMO	X	Y	Z
$b\sigma C_1F$	0.0	4.031	$bd1C_1F$	-0.001	4.300	-0.376
$\ell d1F$	-0.327	5.184	$bd2C_1F$	-0.001	4.303	0.377
$\ell d2F$	0.327	5.184	$\ell d1F$	-0.304	5.187	0.0
$b\sigma C_2H_2$	3.541	2.062	$\ell d2F$	0.304	5.186	0.0
$b\sigma C_3H_3$	3.539	-2.043	$b\sigma C_2H_2$	3.540	2.061	0.0
$b\sigma C_4H_4$	0.0	-4.091	$b\sigma C_3H_3$	3.536	-2.044	-0.001
$b\sigma C_5H_5$	-3.539	-2.043	$b\sigma C_4H_4$	0.0	-4.091	0.0
$b\sigma C_6H_6$	-3.541	2.062	$b\sigma C_5H_5$	-3.538	-2.043	-0.001
$b\sigma C_1C_2$	1.192	1.992	$b\sigma C_6H_6$	-3.541	2.062	0.0
$b\sigma C_2C_3$	2.295	-0.002	bC_1C_2	1.207	1.995	-0.044
$b\sigma C_3C_4$	1.154	-1.984	bC_2C_3	2.190	0.153	-0.382
$b\sigma C_4C_5$	-1.154	-1.984	bC_3C_4	1.159	-1.991	-0.069
$b\sigma C_5C_6$	-2.295	-0.002	bC_4C_5	-1.144	-1.984	-0.104
$b\sigma C_6C_1$	-1.192	1.992	bC_5C_6	-2.291	0.009	-0.116
$b\pi C_1F$	0.0	4.577	bC_6C_1	-1.193	1.989	-0.054
$\pi\ell 23C_1C_2C_3$	1.770	0.805	$bC_1C_2C_3$	1.908	0.552	0.426
$\pi\ell 3C_3C_4C_5$	0.0	-1.879	$bC_3C_4C_5$	-0.097	-1.847	0.173
$\pi\ell 23C_5C_6C_1$	-1.770	0.805	$bC_5C_6C_1$	-1.734	0.867	0.171

each of the substituents and a set of three orbitals in the ring. The latter orbitals can be classified as $\pi l2$ for the *p*-compound, $\pi l3$ for the *m*-compound, and again $\pi l2$ for the *o*-compound. From a symmetry consideration one would expect this result for the *m*- and *o*-compound, although not necessarily for the *p*-form. The charge centroid of the π-orbital of the substituents is always closer to the benzene ring than the charge centroid of the two σ-type bond orbitals. (The data differ only slightly from the data in Table 3.) The position of these charge centroids in the first substituent is the same for the *p*-, and *m*-compound, and only a slight deviation is found for the *o*-compound, which is regarded as numerically insignificant.

In calculation *B* the atoms C_i and C remain linked by a single bond orbital. The CC bond orbitals mix with the π-orbitals of the ring to give only two center bond LMO's (Kekulé structure) for all of the molecules. These LMO's exhibit nearly no distortion.

p-, *m*-, *o*-C_6H_4CNOH and -C_6H_4CNF (Tables 6, 7)

If an OH or a F substituent is introduced into the benzene ring instead of a second CN group the structure of the LMO's changes as can already be anticipated

Table 6. Charge centroids of the LMO's of p-C_6H_4CNOH

LMO	X	Y	Z
A: σ, π			
$b\sigma C_1C$	0.0	3.909	0
$b\sigma C_4O$	-0.048	-4.064	0
$b\pi CN$	0.0	6.271	0
$b\pi C_4O$	0.0	-4.781	0
$\pi l23C_2C_3C_4$	1.748	-0.802	0
$\pi l23C_4C_5C_6$	-1.744	-0.797	0
$\pi l3C_6C_1C_2$	0.006	1.938	0
B: $\sigma+\pi$			
$b\sigma C_1C$	0.0	3.910	0.0
$bd1C_4O$	-0.015	-4.408	-0.394
$bd2C_4O$	-0.012	-4.431	0.397
bC_1C_2	1.147	1.999	-0.080
bC_2C_3	2.247	-0.068	-0.266
bC_3C_4	1.159	-2.026	-0.059
bC_4C_5	-1.185	-1.983	-0.063
bC_5C_6	-2.287	-0.026	-0.164
bC_6C_1	-1.141	1.997	-0.087
$bC_2C_3C_4$	1.799	-0.703	0.324
$bC_4C_5C_6$	-1.740	-0.799	0.228
$bC_6C_1C_2$	-0.027	1.917	0.167

from the results on the monosubstituted benzenes. The case of the OH substituent will be considered first. In calculation A the π-orbital of the CN group remains well localized so that the C atom of this group is linked only via a single bond LMO to the ring. The O atom, on the other hand, is linked to the ring via a σ-type LMO and a π-type LMO which shows considerable delocalization into the ring. The majority of the π-orbitals in the ring are of type $\pi l23$ except for some orbitals of type $\pi l3$ (Tables 6, 7).

In localization B the CN group remains connected to the ring C atom by a single bond orbital, whereas the O atom is always linked to the ring C atom by two equivalent bond orbitals. The structure of the CC bond orbitals is rather complicated due to their distortion. In p-C_6H_4CNOH six two center and three three center bond orbitals are found (Table 6). In the m-compound there are seven two center bond LMO's (two of them are nearly digonally equivalent: $b1C_1C_2$ and $b2C_1C_2$) and two three center bond orbitals (Table 7). The case of the

Table 7. Charge centroids of the LMO's of m-C_6H_4CNOH

LMO	X	Y	Z
A: σ, π			
$b\sigma C_1C$	0.003	3.909	0
$b\sigma C_3O$	3.495	-2.074	0
$b\pi CN$	0.002	6.227	0
$b\pi C_3O$	4.149	-2.395	0
$\pi\ell 23C_1C_2C_3$	1.583	1.132	0
$\pi\ell 23C_3C_4C_5$	-0.167	-1.902	0
$\pi\ell 3C_5C_6C_1$	-1.613	0.963	0
B: $\sigma+\pi$			
$b\sigma C_1C$	0.0	3.907	0.0
$bd1C_3O$	3.812	-2.219	-0.393
$bd2C_3O$	3.837	-2.230	0.397
bC_2C_3	2.345	-0.012	-0.022
bC_3C_4	1.128	-2.014	-0.043
bC_4C_5	-1.149	-1.989	-0.063
bC_5C_6	-2.292	-0.005	-0.093
bC_6C_1	-1.137	2.018	-0.048
$b1C_1C_2$	1.258	1.734	-0.432
$b2C_1C_2$	1.355	1.521	0.455
$bC_3C_4C_5$	-0.034	-1.902	0.107
$bC_5C_6C_1$	-1.654	0.808	0.140

o-compound is very similar except that the double bond is between the atoms C_3 and C_4.

The discussion applies in the same form to the molecules p-, m-, and o-C_6H_4CNF. The only changes compared to the case above are that the π-orbitals in the m-compound are all of type $\pi l23$. In calculation B one encounters seven two center bond LMO's (two of them, between C_5 and C_6, nearly digonally equivalent) and two three center bond LMO's for the p-compound, six two center and three three center bond LMO's for the m-compound, and again seven two center ($b1C_3C_4$ and $b2C_3C_4$ are nearly equivalent) and two three center LMO's for the o-compound.

The difference in this respect compared to the case of C_6H_4CNOH is in significant and is probably due to the difficulty of finding the maximum on a rather flat surface.

Table 8. Charge centroids of the LMO's of m-$C_6H_4(OH)_2$

LMO	X	Y	Z
A: σ, π			
$b\sigma C_1O$	-0.046	4.065	0
$b\sigma C_3O'$	3.498	-2.072	0
$b\pi C_1O$	0.004	4.795	0
$b\pi C_3O'$	4.155	-2.394	0
$\pi l 23 C_1C_2C_3$	1.790	1.033	0
$\pi l 23 C_3C_4C_5$	-0.156	-1.997	0
$\pi l 23 C_5C_6C_1$	-1.807	0.863	0
B: $\sigma + \pi$			
$bd1C_1O$	-0.008	4.442	0.397
$bd2C_1O$	-0.012	4.413	-0.394
$bd1C_3O'$	3.842	-2.228	0.397
$bd2C_3O'$	3.816	-2.217	-0.394
bC_1C_2	1.143	2.020	-0.014
bC_2C_3	2.320	-0.020	-0.014
bC_3C_4	1.133	-2.013	-0.032
bC_4C_5	-1.149	-1.987	-0.091
bC_5C_6	-2.295	-0.002	-0.092
bC_6C_1	-1.177	1.988	-0.033
$bC_1C_2C_3$	1.793	1.035	0.029
$bC_3C_4C_5$	-0.163	-1.994	0.124
$bC_5C_6C_1$	-1.809	0.856	0.125

p-, m-, o-$C_6H_4(OH)_2$ (Table 8)

In calculation A the π-type LMO's cannot be grouped into sets which show a localization with respect to each other. The O atoms are always linked to the C atoms of the ring by a σ-type bond LMO and by a π-type bond LMO, which although more polarized towards the O atoms shows a considerable delocalization into the ring. The remaining π-orbitals are of type $\pi l2$ for the p-compound, $\pi l23$ for the m-compound (Table 8), and $\pi l23$ (which is very close to $\pi l2$) for the o-compound. In calculation B it is found that the O atoms are linked by two bond orbitals to the C atoms of the ring; but these orbitals consist of equivalent orbitals only in the case of the m-compound. In the two other cases the LMO's are distorted from an equivalence. The lone pair orbital is mixing in and acquires some π-character. The CC bond orbitals have a Kekulé-type structure for the p-compound. The equivalence of these orbitals is surprisingly good. In the m-

compound six two center and three three center bond LMO's are found. The structure in the *o*-compound is intermediate. There are three two center bond orbitals between the atoms C_2 and C_3, C_4 and C_5, C_6 and C_1. In addition there are two sets of equivalent banana bond orbitals between the atoms C_3 and C_4 and C_5 and C_6. The remaining bond LMO's between C_1 and C_2 are quite different, both are two center bond orbitals, but one of them has secondary contributions from all atoms in the molecule.

p-, *m*-, *o*-C_6H_4OHF

In the case of the molecule C_6H_4OHF it is again seen that the π-type LMO's of calculation *A* cannot be separated into sets localized relative to each other. Both the O and the F atom are linked by a σ- and a π-bond orbital, which is considerably delocalized into the ring, to the C atoms. The remaining π-orbitals are of type $\pi l23$ for all of the molecules, only in the *o*-compound they come closer to the type $\pi l2$. In calculation *B* it is found that the F atom is always linked to the C atom of the ring by two equivalent bond LMO's, whereas for the O atom this is only the case in the *m*-compound. In the *p*-compound and the *o*-compound the bond orbitals are not equivalent. Their structure is very similar to the case of the molecule $C_6H_4(OH)_2$. The structure of the CC bond orbitals agrees with the one found in the previous case as well. In the *p*-compound a Kekulé-type structure is found, in the *m*-compound six two center and three three center bond LMO's occur, and in the *o*-compound another structure of the LMO's develops. The C atoms C_1 and C_2, C_2 and C_3, C_4 and C_5, C_6 and C_1 are linked by nearly pure σ-type bond orbitals. The C atoms C_3 and C_4 and C_5 and C_6 are linked by digonally equivalent banana bond orbitals. The last bond orbital is a nearly pure three center π-orbital extending over the atoms C_6, C_1, and C_2 (type $\pi l23$, but close to $\pi l3$). This structure is probably also due to the lack of proper numerical convergence.

p-, *m*-, *o*-$C_6H_4F_2$ (Tables 9, 10)

The LMO's of $C_6H_4F_2$ conform with the now familiar structure. In calculation *A* it is found that each F atom is linked by a σ- and a π-type bond orbital to the C atom of the ring. The π-orbitals of the benzene ring are of type $\pi l23$ except for the *p*-compound (Table 9) and the *m*-compound where one of the LMO's is of type $\pi l3$ and except for the *o*-compound (Table 10), where one of the LMO's is of type $\pi l2$. In calculation *B* it is again found that the F atom is always linked to the C atom of the ring by two digonally equivalent banana bond LMO's, which show very little distortion. This is in contrast to the CO bond orbitals discussed above. Apparently the localization procedure is not able to distinguish the CO bond LMO's in these systems well enough from the CC bond LMO's leading to an overall distortion of these bond orbitals, but it can distinguish the CF bond orbitals. These have not been found to show any appreciable deformation. For the molecule $C_6H_4F_2$ the CC bond LMO's show a structure with little distortion. For the *p*-compound a Kekulé-type structure is found, for the *m*-compound six two center and three three center bond orbitals occur and for the *o*-compound the structure is again identical to the one for the *p*-compound.

Table 9. Charge centroids of the LMO's of p-$C_6H_4F_2$

LMO	X	Y	Z
A: σ, π			
$b\sigma c_1F$	0.0	4.026	0
$b\sigma c_4F'$	0.0	-4.026	0
$b\pi c_1F$	0.0	4.644	0
$b\pi c_4F'$	0.0	-4.646	0
$\pi\ell 23c_1c_2c_3$	-1.702	0.787	0
$\pi\ell 3c_3c_4c_5$	1.700	0.790	0
$\pi\ell 23c_5c_6c_1$	0.002	-1.574	0
B: $\sigma+\pi$			
$bd1c_1F$	-0.004	4.333	0.371
$bd2c_1F$	-0.004	4.333	-0.371
$bd1c_4F'$	-0.004	-4.333	0.371
$bd2c_4F'$	-0.004	-4.333	-0.371
$b\sigma c_1c_2$	1.210	2.005	0.0
$b\sigma c_3c_4$	1.210	-2.005	0.0
$b\sigma c_5c_6$	-2.334	0.0	0.0
$bd1c_2c_3$	2.103	0.0	0.479
$bd2c_2c_3$	2.103	0.0	-0.479
$bd1c_4c_5$	-1.069	-1.680	0.453
$bd2c_4c_5$	-1.069	-1.680	-0.453
$bd1c_6c_1$	-1.069	1.680	0.453
$bd2c_6c_1$	-1.069	1.680	-0.453

3. Conclusions

The determination of LMO's for aromatic molecules by the intrinsic localization method of Boys [4] leads to the following conclusions. σ, π-separation in the localization calculation has to be regarded as a constraint. In all cases examined in this work better localized orbitals are obtained, if the MO's of different symmetry are localized together. This is in agreement with previous findings both in aromatic and in non-aromatic molecules [10, 11, 13, 14, 19, 20]. The structure of the LMO's, on the other hand, is simpler in the case of the separate localization of the σ- and π-orbitals. The LMO's of σ-type which have been obtained in this way conform with the now well-known picture of LMO's, and the structure of the LMO's of π-type fully confirms the results of England and Ruedenberg [21, 22] on the Hückel-Wheland type wave functions, in the cases where a comparison can be made. The localized π-orbitals are multi-center bond orbitals,

Table 10. Charge centroids of the LMO's of o-$C_6H_4F_2$

LMO	X	Y	Z
A: σ, π			
$b\sigma C_1F$	0.012	4.021	0
$b\sigma C_2F'$	3.476	2.021	0
$b\pi C_1F$	-0.017	4.629	0
$b\pi C_2F'$	4.017	2.300	0
$\pi l23C_2C_3$	1.847	-0.290	0
$\pi l2C_4C_5$	-0.912	-1.580	0
$\pi l23C_6C_1$	-1.175	1.455	0
B: $\sigma + \pi$			
$bd1C_1F$	-0.006	4.322	0.369
$bd2C_1F$	-0.006	4.322	-0.369
$bd1C_2F'$	3.746	2.156	0.369
$bd2C_2F'$	3.746	2.156	-0.369
$b\sigma C_1C_2$	1.185	2.053	0.0
$b\sigma C_3C_4$	1.168	-2.013	0.0
$b\sigma C_5C_6$	-2.327	0.005	0.0
$bd1C_2C_3$	2.066	-0.154	0.461
$bd2C_2C_3$	2.066	-0.154	-0.461
$bd1C_4C_5$	-1.029	-1.782	0.481
$bd2C_4C_5$	-1.029	-1.782	-0.481
$bd1C_6C_1$	-1.166	1.713	0.460
$bd2C_6C_1$	-1.166	1.713	-0.460

which do mainly extend over two or three centers ($\pi l2$ or $\pi l3$), but have some contribution from most of the C atoms of the benzene ring. If the orbitals of σ- and π-symmetry are localized together, these orbitals mix and localization sometimes leads to distorted and non-equivalent orbitals. The reason for this has been indicated above. This result may be somewhat confusing. But it appears that there are only two different types of structures of the LMO's possible. The first of these structures is a Kekulé-type one with three σ-type single bond and three pairs of digonally equivalent banana bond orbitals. This type is found in the molecules C_6H_6, C_6H_5CN, p-, m-, o-$C_6H_4(CN)_2$, p-$C_6H_4(OH)_2$, p-C_6H_4OHF, p-$C_6H_4F_2$, and o-$C_6H_4F_2$. The second one of these structures corresponds to a set of six two center and another set of three three center bond orbitals, which are more delocalized. These three center bond orbitals have their major contributions from the π-type basis functions and extend over the same centers as the localized π-orbitals of the same molecule do. This type is found for C_6H_5OH, C_6H_5F, p-C_6H_4CNOH, m-C_6H_4CNF, m-$C_6H_4(OH)_2$, m-C_6H_4OHF, and m-

$C_6H_4F_2$. The intermediate structures which have been observed in the remaining molecules and which show a distortion are probably caused by the lack of a proper convergence. One therefore expects that it would be possible to classify the molecules into two classes according to the structure of the LMO's: C_6H_6, C_6H_5CN, $C_6H_4(CN)_2$, and the *p*- and *o*-forms of $C_6H_4(OH)_2$, C_6H_4OHF, and and $C_6H_4F_2$ would give Kekulé-type structures, whereas C_6H_5OH, C_6H_5F, C_6H_4CNOH, C_6H_4CNF, and the *m*-forms of $C_6H_4(OH)_2$, C_6H_4OHF, and $C_6H_4F_2$ would give structures of the second type.

The CX bond orbitals fall into two classes depending on the substituent. The CC(N) bond LMO is always a single bond orbital and the CO and CF bond consists always of two bond orbitals. In the case of the σ,π-separation in the localization calculation the two bond orbitals consist of one σ- and one π-type bond LMO which is more polarized towards the substituent than the σ-bond LMO. In a joint localization of the orbitals digonally equivalent bond orbitals are obtained for the F substituent. The equivalence is poorer for the OH substituent. (In these cases the O lone pair orbital acquires a contribution from the π-type basis functions.) This distortion is not regarded as significant. The CN substituent thus does not interfere strongly with the electron system in the benzene ring, but the OH and F substituents do. In these latter cases the π-electron system cannot be separated into sets localized with respect to each other, but forms one single connected distribution. These structures cannot be regarded as classical structures. The substituent would be positively charged ($\delta+$) independent of whether there is one or two substituents on the ring and the benzene ring would acquire one negative charge (fractional charge $\delta-$) for every substituent, i.e. the ring could be assigned a charge of $2\delta-$. Structures which conform with the octett rule cannot be drawn in these cases in the usual way.

It is not intended to draw definite conclusions from the structure of the LMO's of the aromatic molecules on the *m*-, or *p*- and *o*-directing power of the substituents, but one point should be mentioned. From the structure of the OH and F substituted benzenes, which always show CX double bonds, one expects that the mesomeric structures involving a charge transfer from the substituent to the ring are as important for the C_6H_5OH as for the C_6H_5F molecule. This disagrees with the statement made to the contrary in textbooks on organic chemistry [27], where the corresponding mesomeric forms are considered to be of smaller importance for the halogen compounds.

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