

## CNDO/2 Calculations on Planar and Non-planar Conformations of Anisole, Ethylbenzene, and their *Ortho* Proton $\sigma$ -Complexes\*

ERIK HELGSTRAND

*Research and Development Laboratories, Astra Läkemedel, S-151 85 Södertälje, Sweden*

The non-planar conformations were calculated to be the least stable of anisole and its  $\sigma$ -complex, but the most stable of ethylbenzene and its  $\sigma$ -complex. These differences are discussed as well as corresponding differences in electron populations. The symmetry permits a  $\sigma$ - $\pi$  separation of the molecular orbitals only for conformations planar with respect to the methoxy or ethyl groups. For these conformations the  $\pi$ -electron densities and the  $\pi$ -electron bond order for the particular bond connecting the methoxy or the ethyl group to the ring are given and briefly discussed.

One of the most successful semi-empirical methods developed recently for valence shell calculations is the CNDO/2 (Complete Neglect of Differential Overlap, version 2) method.<sup>1-3</sup> It uses a self-consistent field procedure with explicit consideration of electron repulsions. With this method, good values for the dipole moments of monosubstituted benzenes and energies of rotational barriers in ethane, methylamine, and methanol, have been calculated.<sup>4,5</sup>

The conformational behaviour of the methoxy and the ethyl groups in bromo and methyl substituted 1,3,5-trimethoxy- and 1,3,5-triethylbenzene during electrophilic bromination have been studied experimentally.<sup>6-9</sup> During the formation of the carbon-bromine bond, the nearby methoxy or ethyl groups are forced out of the ring plane, and this will change the ability of these groups to conjugate with the ring. The different isotope effects observed were explained by considering the different conjugative powers of a methoxy and an ethyl group. These arguments were based only on qualitative considerations of the  $\pi$ -electrons involved.

It seemed interesting to apply the CNDO/2 method to the conformational behaviour of a methoxy and an ethyl-substituted benzene in relation to electrophilic aromatic substitution. The simplest significant models seemed to be

\* This work was initiated and part of the calculations performed at School of Chemistry, Georgia Institute of Technology, Atlanta, USA.

anisole, ethylbenzene, and their *ortho* proton  $\sigma$ -complexes. Such a study should give a deeper insight into the electronic behaviour of the important isoelectronic methoxy and ethyl groups substituted on an aromatic ring and, in particular, it should be able to substantiate the qualitative reasoning used in the previous experimental studies. The simple construction of the molecular orbitals in the CNDO/2 method as linear combinations of a minimal set of Slater atomic orbitals should facilitate the interpretation of the results.

#### THEORY AND ATOMIC PARAMETERS

The theory of the CNDO/2 method has been outlined by Pople *et al.*<sup>1-3</sup> The Hartree-Fock matrix elements are

$$F_{\mu\mu} = -\frac{1}{2}(I_{\mu} + A_{\mu}) + [q_A - \frac{1}{2}(P_{\mu\mu} - 1)]\gamma_{AA}$$

$$F_{\mu\nu} = \frac{1}{2}(\beta_A^0 + \beta_B^0) \cdot S_{\mu\nu} - \frac{1}{2}P_{\mu\nu} \cdot \gamma_{AB}$$

where indices  $\mu$  and  $\nu$  refer to atomic orbitals and A and B refer to atoms.  $P_{\mu\nu}$  is an element of the charge density bond order matrix and  $q_A$  is the net charge of atom A. The overlap integrals  $S_{\mu\nu}$  and the electron repulsion integrals  $\gamma_{AB}$  are calculated explicitly from Slater orbitals using only symmetrical  $1s$  or  $2s$  orbitals for the latter integrals. The first term in  $F_{\mu\mu}$  is the average of the atomic ionization potential and the atomic electron affinity, which can be obtained from experimental atomic data. The bonding parameter  $\frac{1}{2}(\beta_A^0 + \beta_B^0)$  in  $F_{\mu\nu}$  depends on empirically chosen atomic parameters  $\beta_A^0$  and  $\beta_B^0$ . The only other necessary parameter is the Slater exponent  $Z$ . All parameters used in the present calculations are given in Table 1.

Table 1. Atomic parameters.

Orbital	$-\frac{1}{2}(I_{\mu} + A_{\mu})$	$\beta_A^0$	$Z$
H1s	7.1761	9.0	1.2
C2s	14.051	21.0	1.625
C2p	5.572	21.0	1.625
O2s	25.39017	31.0	2.275
O2p	9.111	31.0	2.275

The main computer program used in the calculation was coded by Segal and obtained through the QCPE service.<sup>10</sup> The calculations were performed on the Univac 1108 and CDC 6600 computers.

#### GEOMETRIC PARAMETERS

In order to carry out the calculations it is necessary to know the coordinates of all atoms involved. These were calculated from ordinary bond distances and angles obtained from experimental data,<sup>11</sup> when not explicitly mentioned in the

following. The actual transformations to coordinates were performed by a special subprogram COORD<sup>12</sup> fitted to the main program. The investigated structures with the atomic numbering used are shown in Fig. 1. Calculations were performed for two conformations with the dihedral angles C2–C1–O–C7 and C2–C1–C8–C7 equal to 0° and 180°, respectively, and for one conformation with the same dihedral angles equal to 90°. In the following the former conformations will be referred to as planar, while the latter conformation will be referred to as non-planar. Thus in Fig. 1 the conformations shown have the dihedral angles equal to 0°.

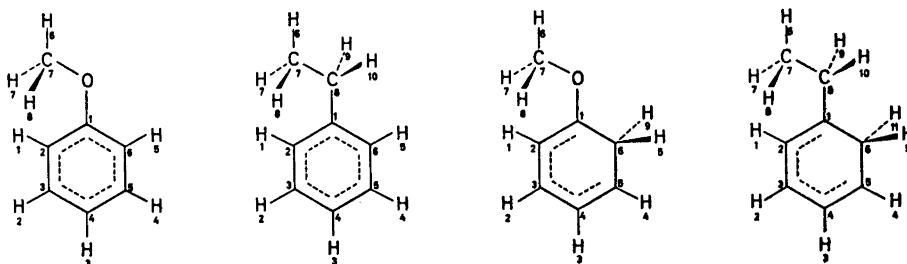


Fig. 1. Structures with numbering system.

In order to estimate the geometry of the  $\sigma$ -complexes, some test calculations on the corresponding benzene  $\sigma$ -complex were carried out. The geometry and hybridization of this  $\sigma$ -complex have been discussed by Melander.<sup>13</sup>

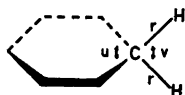


Fig. 2. Benzene proton  $\sigma$ -complex.

The pertinent angles and distances are defined in Fig. 2. For a real hybridization with the hybrid orbitals directed along the bonds, the following relation is valid

$$\cot^2(v/2) = 1 - \cot^2(u/2).$$

Two models were used in the test calculations. In model A, the geometry of the benzene ring was kept unperturbed in the  $\sigma$ -complex, and thus  $u$  is 120°, which gives  $v$  equal to 101.5°. In model B, the angles  $u$  and  $v$  are tetrahedral. All carbon atoms except the tetrahedral one are placed at the same positions as in the unperturbed benzene ring. Thus the tetrahedral carbon atom will be at a distance of 1.48 Å from each of the neighbouring ring carbon atoms. This may be compared with the carbon-carbon distances of 1.40 Å in the unperturbed benzene ring and the corresponding normal single bond value of 1.54 Å. Calculations were performed for different distances  $r$ , while all other C–H distances and the C–C distances were kept constant. The calculated energies as a function of  $r$  for the two models are given in Fig. 3.

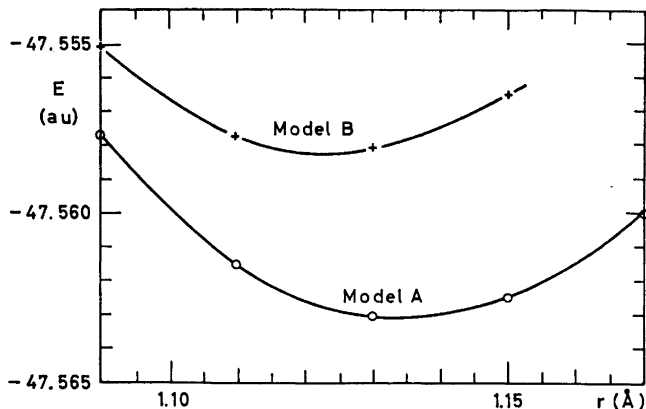


Fig. 3. Energies of benzene proton  $\sigma$ -complexes for different carbon-proton distances, using model A and model B.

Model A gives a slightly lower energy minimum than model B, the difference being 3.1 kcal/mol. At these energy minima  $r$  is 1.135 Å in model A and 1.124 Å in model B, both distances being reasonable for a proton  $\sigma$ -complex. In view of the large difference in the geometry of the ring between the two models, it is somewhat surprising that the corresponding energy difference is so small. In the following calculations on the proton  $\sigma$ -complexes of anisole and ethylbenzene, model A with  $r$  equal to 1.135 Å was used. Although this model is probably somewhat simplified as compared to the real  $\sigma$ -complex, it should be adequate for the present purpose considering the other approximations involved in the calculations. Ideally, of course, all bond distances and angles of each structure (including each conformation!) should be varied until an energy minimum is obtained. This is not feasible with the computers available at present.

#### CALCULATED ENERGIES

The calculated total energies are given in Table 2.

Table 2. Energies (atomic units) of anisole, ethylbenzene, and their ortho proton  $\sigma$ -complexes for different dihedral angles of the methoxy and ethyl groups relative to the ring plane.

Dihedral angle, deg.	Anisole	Ethylbenzene	Anisole $\sigma$ -complex	Ethylbenzene $\sigma$ -complex
0	-74.2334	-64.4879	-74.7185	-64.9647
90	-74.2306	-64.4931	-74.7099	-64.9727
180	—	—	-74.7181	-64.9659

The energy differences between the most stable planar conformation and the non-planar conformation for anisole, its  $\sigma$ -complex, ethylbenzene, and its  $\sigma$ -complex are  $-1.8$ ,  $-5.4$ ,  $3.3$ , and  $4.3$  kcal/mole, respectively. Thus the conformational behaviour of the methoxy group is opposite to that of the ethyl group. The two possible planar conformations of the  $\sigma$ -complexes have nearly the same energy, which implies that any steric repulsion between the methyl groups and the methylene group in the ring is small. Using a molecular orbital method including all valence electrons with parameters taken from self-consistent field calculations of simpler systems, Newton *et al.*<sup>14</sup> calculated the non-planar conformation of ethylbenzene to be  $13.8$  kcal/mole more stable than the planar conformation in qualitative agreement with the present calculation. Experimental evidence of the stability of the planar conformations of ring-protonated anisole has been found.<sup>15</sup> The rotational isomers could be detected by NMR spectroscopy at low temperature. Recently the energy of conjugation between the methoxy group and the ring in anisole has been estimated from experimental data on the heat of formations of Lewis acid complexes to be about  $8$  kcal/mole.<sup>16</sup>

Using the calculated energies of the most stable conformations, the  $\sigma$ -complex of anisole is  $305$  kcal/mole more stable than the initial system consisting of anisole and an isolated proton, while the corresponding value for ethylbenzene and its  $\sigma$ -complex is  $301$  kcal/mole. Thus, in qualitative agreement with general experimental findings anisole may be predicted to be somewhat more reactive than ethylbenzene towards electrophilic substitution. With regard to the found negative formation energies of the  $\sigma$ -complexes, it should be noted that the present calculations refer to an unsolvated state, where the isolated proton has zero energy. In the solvated state these formation energies might very well become positive due to the large negative solvation energy of a proton, especially in highly polar solvents.

#### CALCULATED ELECTRON POPULATION

*General structure of the molecular orbitals.* Each molecular orbital is a linear combination of atomic orbitals taken from a set of  $1s$ ,  $2s$ ,  $2p_x$ ,  $2p_y$ , and  $2p_z$  Slater orbitals. In order to facilitate a possible interpretation in terms of a  $\sigma-\pi$  separation of the electrons, the  $z$ -axis of the orthogonal coordinate system was chosen to be perpendicular to the ring plane of the compounds studied. All structures are isoelectronic, having  $42$  valence electrons, which are distributed over  $21$  molecular orbitals. It should be pointed out that the molecular orbitals obtained (through diagonalization of the Hartree-Fock matrix) are not unique. Any particular orthogonal set based on linear combinations of these molecular orbitals gives the same total energy and electron distribution. However, the molecular orbitals obtained here should be suitable for a general description of the electronic structures.

In all planar conformations the  $xy$ -plane is a symmetry plane, and since all atoms with  $2p$  orbitals lie in this plane, the  $2p_z$  orbitals are orthogonal to all  $2p_x$  and  $2p_y$  orbitals. This symmetry leads to a special set of  $\pi$ -electron molecular orbitals containing only  $2p_z$  atomic orbitals and those  $1s$  atomic

orbitals which have their centres symmetrically under and above the  $xy$ -plane. There is no contribution from  $2p_z$  atomic orbitals in any molecular orbital containing  $2s$ ,  $2p_x$ , and  $2p_y$  atomic orbitals or  $1s$  atomic orbitals with their centres in the  $xy$ -plane. These latter molecular orbitals may be termed  $\sigma$ -electron molecular orbitals. Thus in the planar conformations, a separation of the molecular orbitals into one set of 5  $\pi$ -electron molecular orbitals and one set of 16  $\sigma$ -electron molecular orbitals may be performed. However, this symmetry separation does not imply anything about the relative energies of the molecular orbitals. In all structures there were 7 or 8 consecutive  $\sigma$ -electron molecular orbitals of lowest energy, but at higher energies  $\sigma$ - and  $\pi$ -electron molecular orbitals were intermixed with respect to their energy levels.

The non-planar conformations lack the special symmetry discussed above, and it is then found that all molecular orbitals extend over all atoms and contain various contributions from most of the atomic orbitals including mixtures of the  $2p_x$ ,  $2p_y$ , and  $2p_z$  atomic orbitals of the ring carbon atoms. In these cases it is thus not possible to make any simple  $\sigma$ - $\pi$  separation.

*Dipole moments.* The complete dipole moments, which are approximated by the sums of contributions from net atomic charge densities and atomic polarizations,<sup>2</sup> have been calculated. For the most stable conformations of anisole and ethylbenzene the values 1.49 D and 0.23 D were obtained which may be compared with the corresponding experimental values of 1.36 D and 0.58 D, respectively.<sup>17</sup>

*Total atomic charges.* The atomic charges, obtained by adding the appropriate core charges to the calculated total atomic valence electron densities, are given in Table 3.

Several interesting features in Table 3 can be noted. The total charge of the oxygen atom is always negative, but it becomes less so in going from anisole to its  $\sigma$ -complex, and it is also less negative for the planar than the non-planar conformation. Thus, the basicity of the oxygen atom is largest for the non-planar conformation, and reactions, which are dependent on this basicity, such as ether cleavage, should be facilitated by steric hindrance of the methoxy group. This is supported by kinetic data.<sup>18</sup> The corresponding charge of C8 in the ethyl group is slightly positive in ethylbenzene and becomes slightly negative in its positively charged  $\sigma$ -complex. The difference in the charge of C8 between the planar and non-planar conformations is also opposite to the one observed for the oxygen atom in anisole and its  $\sigma$ -complex. In the  $\sigma$ -complexes of both anisole and ethylbenzene more than half of the positive overall charge is distributed among the hydrogen atoms. The increase of charge is about the same for all hydrogen atoms, including those of the methyl group, in going from anisole and ethylbenzene to their  $\sigma$ -complexes. However, there are some interesting minor differences between the charges of H6, H7, and H8, and between H9 and H10, depending on their positions relative to neighbouring atoms. This might be due mainly to non-bonding interactions. The charges of the carbon atoms of the rings and the nearby C8 are alternating, and a change of the charge of one atom is accompanied with an opposite change of the charges of the neighbouring atoms.

*$\pi$ -Electron densities and bond orders.* For the planar conformations,  $\pi$ -electron densities may be calculated as the total electron populations of the

Table 3. Total atomic charges of anisole, ethylbenzene, and their  $\sigma$ -complexes for different dihedral angles of the methoxy and ethyl groups relative to the ring plane.

Atom	Anisole with dihedral angles		Ethylbenzene with dihedral angles		Anisole $\sigma$ -complex with dihedral angles		Ethylbenzene $\sigma$ -complex with dihedral angles		
	0°	90°	0°	90°	0°	90°	0°	90°	180°
O	-0.219	-0.229			-0.174	-0.197	-0.174	-	-
C1	0.193	0.185	0.042	0.041	0.319	0.326	0.174	0.187	0.174
C2	-0.050	-0.050	-0.012	-0.017	-0.098	-0.089	-0.057	-0.061	-0.055
C3	0.027	0.025	0.009	0.016	0.172	0.168	0.170	0.162	0.166
C4	-0.023	-0.013	-0.005	-0.005	-0.036	-0.039	-0.032	-0.037	-0.030
C5	0.028	0.025	0.010	0.016	0.124	0.131	0.120	0.128	0.125
C6	-0.060	-0.050	-0.010	-0.017	-0.063	-0.069	-0.047	-0.042	-0.045
C7	0.134	0.139	-0.006	-0.003	0.129	0.138	-0.012	-0.002	-0.018
C8	-	-	0.011	0.016	-	-	-0.018	-0.006	-0.023
H1	0.007	0.007	-0.004	-0.008	0.062	0.069	0.056	0.053	0.052
H2	-0.005	-0.006	-0.008	-0.008	0.055	0.057	0.057	0.054	0.054
H3	-0.006	-0.006	-0.008	-0.008	0.058	0.059	0.057	0.057	0.056
H4	-0.007	-0.006	-0.008	-0.008	0.056	0.055	0.052	0.052	0.052
H5	0.005	0.007	-0.008	-0.008	0.154	0.151	0.149	0.149	0.151
H6	-0.002	-0.001	-0.008	-0.002	0.048	0.049	0.035	0.045	0.043
H7	-0.011	-0.013	0.002	0.004	0.020	0.019	0.020	0.027	0.010
H8	-0.011	-0.013	0.002	0.004	0.020	0.008	0.020	0.015	0.010
H9	-	-	0.000	-0.006	0.154	0.163	0.050	0.044	0.064
H10	-	-	0.000	-0.006	-	-	0.050	0.027	0.064
H11	-	-	-	-	-	-	0.149	0.147	0.151

Table 4.  $\pi$ -Electron densities in the planar conformations of anisole, ethylbenzene, and their  $\sigma$ -complexes.

Atom	Anisole	Ethylbenzene	Anisole $\sigma$ -complex with dihedral angle		Ethylbenzene $\sigma$ -complex with dihedral angle	
			0°	180°	0°	180°
O	1.907	—	1.821	1.816	—	—
C1	0.947	0.975	0.730	0.735	0.726	0.728
C2	1.063	1.022	1.117	1.108	1.076	1.074
C3	0.975	0.991	0.729	0.735	0.719	0.726
C4	1.043	1.015	1.052	1.048	1.049	1.046
C5	0.974	0.991	0.810	0.817	0.785	0.794
C6	1.066	1.020	0.999	0.995	0.987	0.987
C7	0.977	0.978	1.007	0.997	0.995	0.983
C8	—	0.960	—	—	0.991	0.999
H5	—	—	0.362	0.366	0.358	0.357
H7	0.524	0.511	0.505	0.509	0.502	0.507
H8	0.524	0.511	0.505	0.509	0.502	0.507
H9	—	0.513	0.362	0.366	0.476	0.468
H10	—	0.513	—	—	0.476	0.468
H11	—	—	—	—	0.358	0.357

$2p_x$  and  $1s$  atomic orbitals constituting the  $\pi$ -electron molecular orbitals defined previously. These electron densities are given in Table 4.

The  $\pi$ -electron densities of the carbon atoms in the rings follow the same general pattern as the total electron densities (*cf.* Table 3) although the variations are somewhat larger. Some delocalization of the positive charge of the anisole  $\sigma$ -complex to the oxygen atom apparently takes place, while there is no such delocalization to C8 of the  $\sigma$ -complex of ethylbenzene. It is interesting to note the large and nearly equal participation of the atomic orbitals of H7 and H8 of all compounds and the similar participation of the atomic orbitals of H9 and H10 of ethylbenzene and its  $\sigma$ -complex. In the  $\sigma$ -complexes of both anisole and ethylbenzene there are also equal and fairly large participations from the atomic orbitals of H5 and H9 or H11, respectively. In going from ethylbenzene to its  $\sigma$ -complex, some electron density of the atomic orbitals of H9 and H10 is lost.

$\pi$ -Electron bond orders between  $2p_x$  atomic orbitals can be defined for the planar conformations. Of particular interest is the  $\pi$ -electron bond order of the bond linking the methoxy and the ethyl group to the rings. There is very little difference between the two possible planar conformations of the  $\sigma$ -complexes. For a dihedral angle 0°, these bond orders are 0.533 and 0.874 for anisole and its  $\sigma$ -complex, and 0.415 and 0.512 for ethylbenzene and its  $\sigma$ -complex. The different behaviour of the methoxy and the ethyl groups is thus also shown here and agrees with simple qualitative predictions based on the conjugative abilities of a methoxy and an ethyl group.



## CONCLUSIONS

Although very good quantitative results of CNDO/2 calculations pertinent to the present work have been obtained,<sup>4,5</sup> the scheme of the CNDO/2 method is too simple to enable precise quantitative predictions. It should also be noted that this method is quite sensitive to the geometric parameters. However, the following qualitative conclusions should be valid.

The non-planar conformation is more stable than the planar conformations for ethylbenzene and its  $\sigma$ -complex. Thus, a steric hindrance induced during aromatic substitution, which prevents the ethyl group lying in the ring plane, should have little effect on the energy. Contrary to this, the same type of steric hindrance induced during aromatic substitution of anisole should increase the energy. These effects should also be present in 1,3,5-triethylbenzene and 1,3,5-trimethoxybenzene although there is some indication<sup>15</sup> that the effect may be smaller for 1,3,5-trimethoxybenzene than for anisole. Assuming that the behaviour of the activated complexes are similar to the behaviour of the  $\sigma$ -complexes, these findings support the conclusions drawn previously.<sup>6-9</sup>

The structure of the molecular orbitals and their relative energies show that it is not possible to make a  $\sigma$ - $\pi$  separation of the valence electrons based on an energy criterion, even if such a separation is possible with respect to symmetry. The molecular orbitals obtained for the non-planar conformations emphasize the necessity of including all valence electrons in the treatment and show the difficulties of such concepts as inductive and conjugative effects. In these cases the molecular orbitals extend over the whole molecule, and even if it would be possible to transform these orbitals into more localized orbitals, there would still be many non-bonded interactions of great importance, for instance those between the atoms of the methyl groups and the ring carbon atoms. It should also be noted that the  $\pi$ -electron molecular orbitals separated on the basis of symmetry alone extend over all those atoms where the symmetry allows participation of the atomic orbitals, irrespective of whether such atoms are part of an unsaturated or a saturated system.

The present study shows the feasibility of applying the CNDO/2 method to relatively complex molecules and their conformational behaviour. Due to the simple construction of the molecular orbitals, an easily interpreted picture of the electronic structure is obtained.

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