Electrophilic Aromatic Triphenylmethylation. Self-Consistent Field–Molecular Orbital Calculations on Phenol, Alkoxybenzenes, and Ortho Alkoxyphenols

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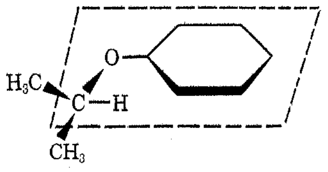
SCF–MO calculations were carried out on phenol, phenolate, anisole, phenetole, isopropoxybenzene, 2,6-dimethylanisole, and ortho alkoxyphenols using the CNDO/2 approximation. Experimental results on triphenylmethylation have established the sequence anisole < phenol < phenetole < isopropoxybenzene of increasing reactivity. The results of the calculations are in agreement with the generally accepted inductive release sequence: *i*-Pr > Et > Me > H. The calculations indicate that the trityl ion does not attack directly at the para position, but that the reaction proceeds *via* a charge-transfer-type transition state. 2,6-Dimethylanisole where the methoxy group is twisted 90° out of the plane could not be tritylated. This result is in agreement with the decrease in overlap between the empty orbital of the trityl ion and the HOMO of the 2,6-dimethylanisole as compared to anisole. The results on phenol and ortho alkoxyphenols suggest the importance of hydrogen-bond formation in the tritylation of these compounds.

In the previous paper[2] we have reported SCF–MO calculations on a series of anilines. The results of these calculations showed a quantitative correlation between the HOMO coefficients, the HOMO energy levels, and the relative reactivity of these compounds toward the trityl carbonium ion. The success of these calculations encouraged us to carry out further CNDO/2 calculations on a series of compounds for which rate data for tritylation were already available.[3] Rate studies on phenol and a series of its alkyl ethers have been reported by Chuchani, Díaz, and Zabicky,[3a] and on ortho alkoxyphenols by Barroeta, Chuchani, and Zabicky.[3b] We wish now to report CNDO/2 calculations on these compounds.

Results and Discussion

The CNDO/2 calculations[4] were carried out using the following bond distances and angles: C_{ar}–C_{ar}, 1.40 Å; C_{ar}–H, 1.085 Å; C_{ali}–C_{ali}, 1.54 Å; C_{ar}–O, 1.36 Å; O–CH_3, 1.35 Å; C_{ali}–H, 1.09 Å; O–H, 0.958 Å; C_{ar}–O–H, angle and tetrahedral angles, 109.5°; all other angles, 120°.

The results on phenol and alkoxybenzenes are summarized in Chart I. In all these calculations a planar geometry was assumed. For isopropoxybenzene structure i was found to be most stable.



i

In our previous work[2] on anilines we have found that the frontier orbital theory[5] gave a good description of the experimental results. One of the reactivity indices proposed by Fukui[5] is the superdelocalizability (eq 1)

$$S_r^{(E)} = 2 \sum_{i}^{\text{occ}} \frac{c_r^{(i)2}}{\alpha - \epsilon_i}(-\beta) \qquad (1)$$

where $c_r^{(i)}$ is the coefficient of the *i*th MO at atom *r*, α is the LUMO (lowest unoccupied molecular orbital) energy level of the attacking electrophile, ϵ_i is the energy of the *i*th MO. The superdelocalizability is expressed in units of β, the resonance integral. Fukui[5] has shown that the dominant term in the sum of eq 1 is the frontier term, eq 2. Equation 2 shows that the

$$S_r^{(E)} = 2 \frac{c_r^{(\mathrm{HO})2}}{\alpha - \epsilon_{\mathrm{HO}}}(-\beta) \qquad (2)$$

relative reactivity of a series of compounds depends on the HOMO coefficient $c_r^{(\mathrm{HO})}$ and the HOMO energy level ϵ_{HO}.

Through the work of Chuchani, *et al.*,[3] the following reactivity sequence was established: anisole < phenol < phenetole < isopropoxybenzene. Unlike the reactivity sequence in the aniline series,[2] which was determined by the nonkinetic competition method, the reactivity of the alkoxybenzenes and phenol was determined by direct measurement of second-order rates. The results of our calculations show that the biggest HOMO coefficients (which are all p_z coefficients) are at the oxygen and at the para position. The HOMO coefficient at the para position decreases in the series OH > OCH_3 > OC_2H_5 > $OCH(CH_3)_2$. A direct attack at the para position therefore appears to be unlikely since it would lead to a reactivity sequence contrary to the experimental results. However the HOMO coefficient at the oxygen increases in the above series and so does the HOMO energy level (*i.e.*, becomes less negative). This corresponds to an increase in $S_r^{(E)}$. The importance of the HOMO energy level is evident from the high solute selectivity of the trityl ion. Trityl does react with aniline (HOMO level: −0.4424 au),[2] *N*-methylaniline (−0.4373),[2] *N*,*N*-dimethylaniline (−0.4296),[2] anisole (−0.4477), phenetole (−0.4455), isopropoxybenzene (−0.4353), and phenol (−0.4556), but does not react with toluene (−0.4730),[2] chlorobenzene (−0.4677)[2] or nitrobenzene (−0.4741).[2]

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[1] The Puerto Rico Nuclear Center is operated by the University of Puerto Rico for the U. S. Atomic Energy Commission under Contract AT-(40-1)-1833.

[2] M. K. Eberhardt and G. Chuchani, *J. Org. Chem.*, **37**, 3649 (1972).

[3] (a) G. Chuchani, H. Díaz, and J. Zabicky, *ibid.*, **31**, 1573 (1966); (b) N. Barroeta, G. Chuchani, and J. Zabicky, *ibid.*, **31**, 2330 (1966).

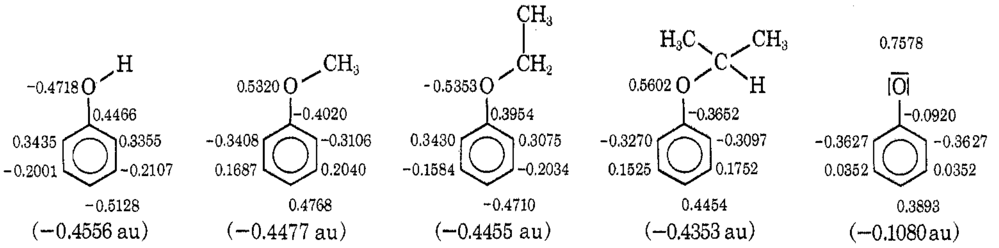
[4] The program was obtained from the Quantum Chemistry Program Exchange, Bloomington, Ind. The method is described by J. A. Pople and D. L. Beveridge in "Approximate Molecular Orbital Theory," McGraw Hill, New York, N. Y., 1970.

[5] For a recent review, see F. Fukui in *Topics Current Chem.*, **15**, 1 (1970).

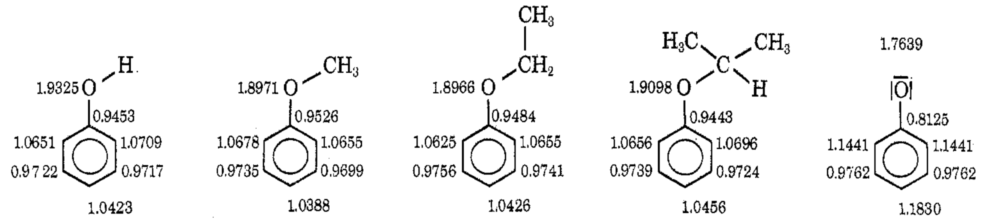
Chart I

CNDO/2 Calculations on Phenol, Phenolate, and Alkoxybenzenes

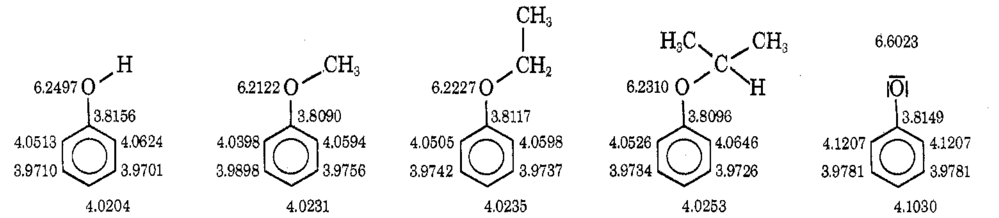
p_z HOMO Coefficients and HOMO Energy Levels



p_z–π Densities



Total Electron Densities

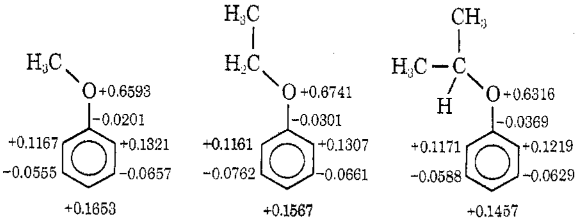


In addition to HOMO coefficients Chart I shows p_z–π densities and total electron densities. The p_z–π densities cannot explain the exclusive attack at the para position, since the ortho positions have a higher p_z–π density. As discussed previously[2] the increase in para p_z–π density in the series anisole < ethoxybenzene < isoproxybenzene means increasing stability of the σ complex. One may be inclined to attribute the exclusive para substitution to steric hindrance in the ortho position. This however cannot be the only reason especially in the case of phenol since *m*-aminophenol was found to react para to the amino and ortho to the hydroxyl group.[6]

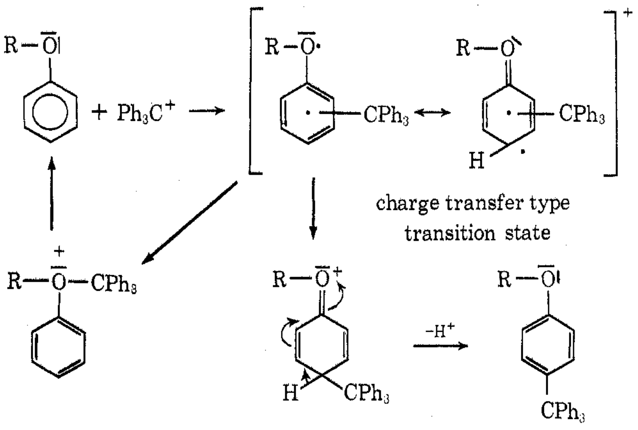
The total electron densities show that the highest net negative charge is at the oxygen atoms. At large distances the trityl ion will be attracted to the point of highest net negative charge. As the trityl ion approaches its empty orbital (LUMO) begins to overlap with the HOMO of the aromatic forming a charge-transfer-type transition state, which then forms a σ bond either at the oxygen or at the para position. The alkoxybenzene radical ion has the highest spin density at the oxygen and at the para position (Chart II). Only a σ bond formation at the para position leads to a stable final product (Scheme I).

Chart II

p_z Spin Densities of Alkoxybenzene Radical Ions



Scheme I



According to the generally accepted inductive release sequence, *i*-Pr > Et > Me > H, and to our calculations, phenol should react slower than any of the alkoxybenzenes; however, experimentally it was found that phenol falls between anisole and phenetole in reactivity.[3a] The phenolate ion with a very high HOMO coefficient at the oxygen and a very high lying HOMO energy level should react faster than any of the alkoxybenzenes. This disagreement suggests, as argumented with supporting evidence in previous work,[3] hydrogen-bond formation between the phenol molecules and the solvent. This hydrogen-bond formation may sufficiently increase the HOMO coefficients at the oxygen to render phenol more reactive

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[6] G. Chuchani and J. Zabicky, *J. Chem. Soc. C*, 297 (1966).

TABLE I

EFFECT OF ROTATION

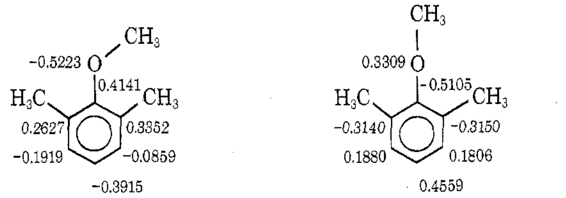
	Phenol			
Angle of OH bond with plane of ring, deg	0	30	60	90
Total energy, au	−65.5523	−65.5509	−65.5487	−65.5479
HOMO energy level, au	−0.4556	−0.4582	−0.4653	−0.4706
Max HOMO coefficient at oxygen (p_z)	−0.4718	−0.4362	−0.3496	0.2938
Max HOMO coefficient at para position (p_z)	−0.5128	−0.5112	−0.5141	0.5294
	Anisole			
Angle of OCH_3 group with plane of ring, deg	0	30	60	90
Total energy, au	−74.2178	−74.2165	−74.2162	−74.2162
HOMO energy level, au	−0.4477	−0.4490	−0.4572	−0.4677
Max HOMO coefficient at oxygen (p_z)	0.5320	−0.4928	0.3909	0.3413
Max HOMO coefficient at para position (p_z)	0.4768	−0.4617	0.4486	0.5203
	Ethoxybenzene			
Angle of OC_2H_5 group with plane of ring, deg	0	30	60	90
Total energy, au	−82.9286	−82.9268	−82.9266	−82.9265
HOMO energy level, au	−0.4455	−0.4465	−0.4555	−0.4650
Max HOMO coefficient at oxygen (p_z)	−0.5353	−0.4992	−0.4044	−0.3520
Max HOMO coefficient at para position (p_z)	−0.4710	−0.4589	−0.4614	−0.5174

than anisole. Further evidence for hydrogen-bond formation will be presented below.

Table I shows the effect of rotation of the alkoxy groups on the HOMO coefficients. While the HOMO coefficients at the para position stay almost constant the coefficients at the oxygen change much more drastically. It was therefore of interest to study the tritylation of an alkoxybenzene in which the alkoxy group is twisted out of the plane of the ring. The tritylation of 2,6-dimethylanisole was tried by two common methods but failed. The calculations are shown in Chart III. If we compare the HOMO coefficients of anisole with the twisted form of 2,6-dimethylanisole we realize again that direct attack at the para position could not explain this difference in reactivity. In the twisted 2,6-dimethylanisole we find a much smaller HOMO coefficient at the oxygen than in anisole. The decreased overlap at the oxygen must be responsible for the failure to react. Even if a charge-transfer-type transition state would be formed σ-bond formation appears unlikely owing to the very small spin densities in the para position of the twisted 2,6-dimethylanisole radical ion (see Chart IV).

CHART III

CNDO/2 CALCULATIONS ON 2,6-DIMETHYLANISOLE[a]



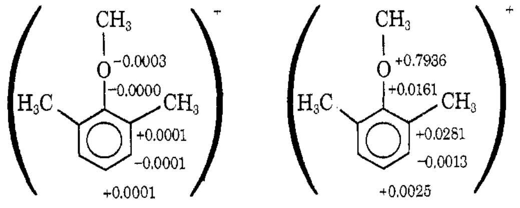
HOMO energy level, −0.4226 au HOMO energy level, −0.4507 au

E_{total} = −91.5985 au E_{total} = −91.6300 au

[a] Maximum (p_z) HOMO coefficients, HOMO energy levels, and total energies of 2,6-dimethylanisole with OCH_3 group in the plane of the ring (left) and twisted by 90° (right).

CHART IV

SPIN DENSITIES IN 2,6-DIMETHYLANISOLE RADICAL ION



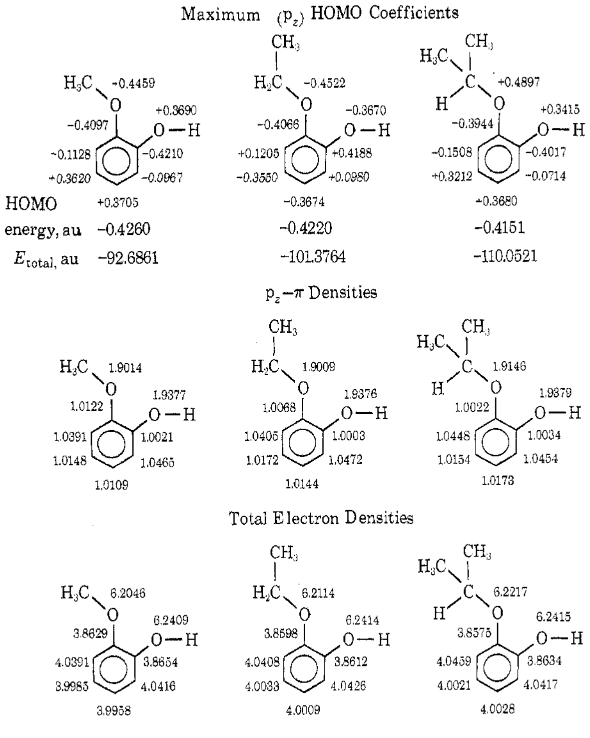
p_z spin densities maximum (p_y) spin densities

Evidence for the importance of hydrogen bonding in the tritylation of phenols can also be deduced from the tritylation of ortho alkoxyphenols. On the basis of the experimentally established reactivity sequence one would expect that *o*-ethoxyphenol and *o*-isopropoxyphenol react para to the alkoxy group. All ortho alkoxyphenols react para to the OH group.[3b]

Calculations were carried out on the nonhydrogen-bonded ortho alkoxyphenols (Chart V) and the hy-

CHART V

CNDO/2 CALCULATIONS ON NONHYDROGEN-BONDED ALKOXYPHENOLS

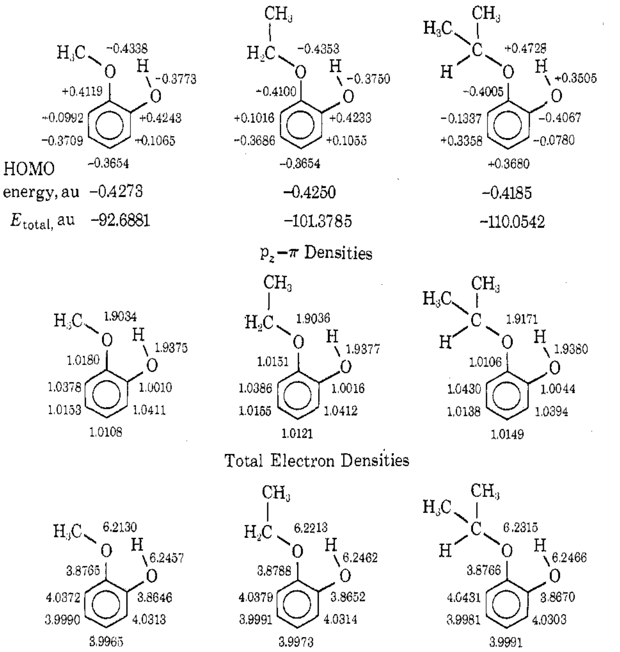


drogen-bonded structures (Chart VI). In all cases the HOMO (highest occupied molecular orbital) was a pure $p_z-\pi$ orbital. In addition to the HOMO coefficients the charts list the $p_z-\pi$ densities and the total electron densities. We have shown previously for the case of anilines[2] and alkoxybenzenes that σ-bond formation takes place at the ring position which has the highest spin density in the radical ion. As has been shown for alkoxybenzenes and anilines[2] the highest spin density in the radical ion is always at the position of the maximum HOMO coefficient in the neutral molecule. Chart V shows that the maximum HOMO coefficient at the nonsubstituted ring carbons is at the position para to the alkoxy group and substitution would be expected at that position contrary to experimental results.

CHART VI

CNDO/2 CALCULATIONS ON HYDROGEN-BONDED ALKOXYPHENOLS

Maximum (p_z) HOMO Coefficients



The calculation of the hydrogen-bonded structures (Chart VI), however, show that the maximum HOMO coefficient at the unsubstituted ring carbons is now para to the OH group for guaiacol and *o*-ethoxyphenol. This means that hydrogen bonding increases the directive power of the OH group. For *o*-isopropoxyphenol the reaction would still be expected to take place para to the isopropoxy group, but we can see that compared to the nonhydrogen-bonded structure the HOMO coefficient at the position para to the OH group has increased. A stronger hydrogen bond may give the desired result. An increase in the strength of the hydrogen bond from guaiacol to isopropoxyphenol is to be expected because of the increasing total electron density at the oxygen of the alkoxy group. The distance O—H···OR in the structures of Chart VI is 2.26 Å. We have found that by shortening this distance to 1.60 Å we can indeed obtain the maximum HOMO coefficient para to the OH group. However, owing to the required distortion of the C_{ar}–O–H angle the total energy also increases considerably. Hydrogen-bond formation with the solvent does not require any such deformation of the C_{ar}–O–H angle.

Experimental Section

Triphenylmethanol (Matheson Coleman and Bell), anisole (Fisher), and 2,6-dimethylanisole (Aldrich) were purified by crystallization or distillations under vacuum. Triphenylmethyl perchlorate was prepared as described before.[3a] Ir spectra were determined with a Perkin-Elmer 337. For nmr spectra a Varian A-60 was used. Mass spectra were determined in a Hitachi Perkin-Elmer RMU-6H instrument. Melting points were taken with a Fisher-Johns apparatus.

Attempts to tritylate 2,6-dimethylanisole with triphenylmethyl perchlorate alone and with triphenylmethanol in an acetic acid–hydrochloric acid mixture resulted in no reaction.

Competition of Anisole and 2,6-Dimethylanisole. Method A.—Anisole (0.05 mol), 2,6-dimethylanisole (0.05 mol), and triphenylmethyl perchlorate (0.005 mol) were heated at 80–85° for 19 hr under nitrogen and in absence of light. The reaction mixture was dissolved in acetone, diluted with water, extracted with ether, and dried. The ether and anisoles were distilled and the residue was dissolved in small amounts of chloroform. The compounds were separated with a neutral alumina column chromatography (30 g, Woelm, grade I) and eluted with petroleum ether and then with a benzene–chloroform mixture (2:1 by volume). The only product obtained was 4-methoxytetraphenylmethane, 81.4% [mp 194° (lit.[7] mp 194–195°)]. This product was identified by mixture melting point and ir, nmr, and mass spectral comparison with an authentic sample.

Method B.—A mixture of anisole (0.10 mol), 2,6-dimethylanisole (0.10 mol), triphenylmethanol (0.01 mol), glacial acetic acid (100 ml), and hydrochloric acid (8 ml) was refluxed for 1 week, diluted with water, extracted with ether, and dried. The ether and excess of anisole were distilled and residue was treated as described in method A. Products and yields follow: recovered triphenylmethanol, 87.2%, and 4-methoxytetraphenylmethane, 11.4%.

Registry No.—Phenol, 108-95-2; phenolate, 3229-70-7; anisole, 100-66-3; phenetole, 103-73-1; isopropoxybenzene, 2741-16-4; 2,6-dimethylanisole, 1004-66-6; guaiacol, 90-05-1; *o*-ethoxyphenol, 94-71-3; *o*-isopropoxyphenol, 4812-20-8.

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[7] C. A. MacKenzie and G. Chuchani, *J. Org. Chem.*, **20**, 336 (1955).