charge transfer from the n orbital on the 5-substituent to the LUMO of the dienophile. However, this mode of nonbonded interaction may occur at the cost of more significant interaction between the π HOMO of the diene and the π LUMO of the dienophile indispensable to the cycloaddition. The HOMO of the cyclopentadiene with an n orbital at the 5 position is out-of-phase combination of the π HOMO and the n orbital. Accordingly, if the nonbonded attraction occurs effectively, or if the LUMO of dienophile is in-phase combined with the n-orbital component of the HOMO, the antibonding nature appears between the π HOMO component of diene and the LUMO of dienophile. This suggests that the nonbonded attraction of the n orbital with the reaction center of the dienophile disfavors the leading interaction in the Diels–Alder reactions.

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Molecular Orbital Studies of the Protonation of the Methylanisoles

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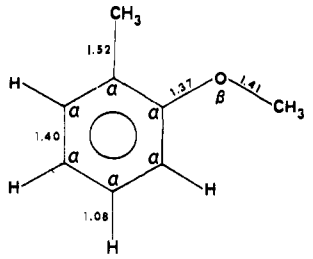
Abstract: Application of the STO-3G method to the energetics of protonation of the ambident methylanisoles shows the predominance of ring protonation for all three isomers. The method further indicates that oxygen protonation is only competitive for the para isomer. Comparison of these results with those for the methylphenols allows prediction of differences between the hydroxy and methoxy substituents in a typical system, and the predictions are in close accord with experimentally well known trends.

We report herewith a study of the site of protonation of the methylanisoles using the STO-3G method.[1] The methylanisoles are of special interest as a test of theory because the site of protonation experimentally is not always the same as in the corresponding methylphenols. We have previously performed similar calculations on the methylphenols using both the STO-3G and INDO programs.[2] The ab initio results for the methylphenols correctly predicted the order of stability of the neutral compounds and also the favored protonation sites. The INDO method failed to yield results concordant with experiment for either the neutral methylphenols or the protonated forms of these compounds. In light of these shortcomings of the semiempirical method, we have elected to perform only STO-3G calculations in the present study.

The geometries used for the neutral methylanisoles are shown in Figure 1. The aromatic ring was constructed from standard model geometries.[3] Since results on the methylphenols agree with experiment and those on proton affinity differences of alkylbenzenes are within 600 cal mol^{-1} of observed differences,[4] we assume that the standard model geometry is a reliable guide for the study of these compounds. We selected substituent geometries (the C–O bond lengths and the angle β) on the basis of INDO energy minimization, the agreement between INDO results[5] and STO-3G results[6] for bond lengths in hydrocarbon ions being within 0.01 to 0.02 Å. The same standard substituent bond lengths and angles were used for all three isomers.

Figure 2 represents the geometries used for the ring-protonated methylanisoles. The ring structure is based upon the model for protonated benzene reported by Hehre et al.,[4] with the exception noted in ref 7. The substituent geometries are the same as for the neutrals and are constant for all protonated forms.

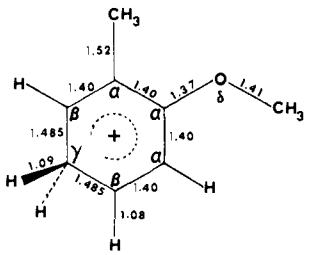
The geometries for the oxygen-protonated forms are illustrated in Figure 3. The aromatic ring is assumed to have the same model geometry as the neutral compounds. The substituent geometries were again chosen on the basis of INDO energy minimization. Unlike the methylphenols,[2] there was



α = 120°

β = 112°

Figure 1. Molecular geometry for the neutral methylanisoles.



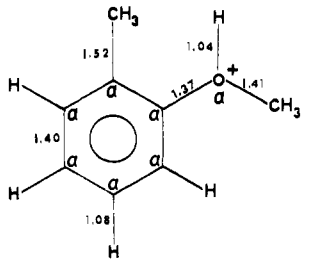
α = 120°

β = 125.26°

γ = 109.47°

δ = 112°

Figure 2. Molecular geometry for the ring-protonated methylanisoles.



α = 120°

Figure 3. Molecular geometry for the oxygen-protonated methylanisoles.

no observed expansion in the ring carbon–oxygen bond length with protonation at the oxygen. The protonated ether substituent was taken to be coplanar with the aromatic ring, with bond angles of 120°, tetrahedral being of higher energy. Here again, the substituent geometries are identical for all three isomers.

Energies

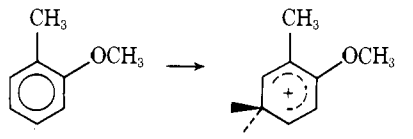
Table I lists, in atomic units, the energies of the methylanisoles as neutrals and also the energies of each reasonable protonated form of the methylanisoles. Attachment of the proton at each ring carbon and also at oxygen was considered. The calculated energy of each form in excess of that of the most stable form is given in kilocalories per mole in parentheses. The proton affinity is defined as the enthalpies of the reactions (reaction 1), where MH^+ is the most stable protonated form.

$$MH^+ \rightarrow M + H^+ \qquad (1)$$

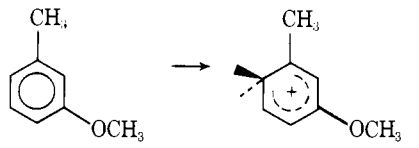
These results for the methylanisoles are mirrored in solution work, and the correspondence suggests that solvent effects do not mask the intrinsic basicity of the sites in general. For *o*-methylanisole, the NMR studies of Olah and Mo indicate that Scheme I occurs in four different superacid systems.[8] Our calculations agree with this process and further suggest that the ipso form (protonation at position 1) is also of low energy. This tendency was also observed for *o*-methylphenol, with protonation at position 5 favored by 1.9 kcal mol^{-1} over protonation at position 1.[2]

For *m*-methylanisole, Scheme II has been observed in three different superacid systems.[8] The STO-3G results indicate that protonations at position 2 and at position 6 are essentially indistinguishable. We are unaware of any solution work that has identified protonation at position 2 as a competitive process.

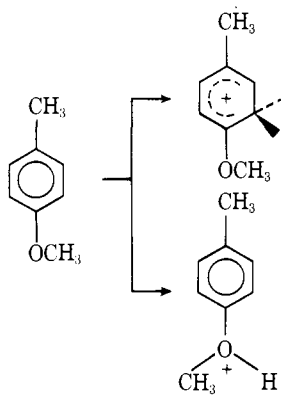
Scheme I



Scheme II



Scheme III



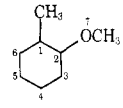
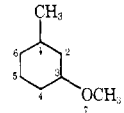
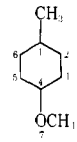
Perhaps Scheme II is favored experimentally as a result of steric factors or because of solvent interactions.

For *p*-methylanisole, oxygen protonation is experimentally found to compete with ring protonation (Scheme III). The ratio of products depends upon the particular solvent employed.[8,9] In one system, $HF–BF_3$ at −85 °C, protonation occurs solely on oxygen.[10] The STO-3G results are in excellent agreement with Scheme III, with protonation at position 3 most favored. Oxygen protonation is of higher energy, but it is apparent that oxygen protonation is more probable in *p*-methylanisole than in either *o*- or *m*-methylanisole. In STO-3G calculations on *p*-methylphenol, two ring-protonated forms (at positions 1 and 3) were found to be more favorable than oxygen protonation. The increased stability of oxygen protonation for *p*-methylanisole can be partially reconciled by examination of the energies of all the lower-energy forms in all isomers of the methylphenols and their methyl ethers. In every case, protonation on oxygen in the methylanisoles becomes more competitive with protonation on carbon than in the methylphenols. We cannot make quantitative comparisons between the two sets of compounds because of the slight difference in geometry alluded to in ref 7. Nevertheless, even when the necessary corrections to the methylphenol geometries are taken into account, the oxygen-protonated forms are still several kilocalories per mole less competitive than in the corresponding methyl ethers.

There are further noteworthy correlations with practice. Of all the protonated forms, the most stable one is the protonated meta isomer in which the proton is added ortho to both the methyl and methoxy groups. The meta isomer with protonation para to methoxy and ortho to methyl is of comparable stability. This is just what would be predicted from experience by organic chemists for in their terms, the donating effects of the methyl and methoxy substituents are cooperative at these positions.

If one compares the energy differences between various ring-protonated forms and the most stable protonated form for *m*-methylphenol and *m*-methylanisole (the value in parentheses in Table I), one finds that, position for position, they

Table I. Calculated Energies of Methylanisoles and Protonated Methylanisoles

			
	E,[a] (ΔE)[b]	E,[a] (ΔE)[b]	E,[a] (ΔE)[b]
Neutral	−378.847 34	−378.845 85	−378.851 47
Protonated at			
1	−379.273 11 (1.4)	−379.239 60 (27.3)	−379.271 36 (3.8)
2	−379.228 94 (29.1)	−379.283 04 (0)	−379.250 81 (16.7)
3	−379.270 00 (3.3)	−379.220 58 (39.2)	−379.277 41 (0)
4	−379.256 87 (11.6)	−379.279 70 (2.1)	−379.231 60 (28.8)
5	−379.275 32 (0)	−379.245 61 (23.5)	−379.277 41 (0)
6	−379.252 00 (14.6)	−379.282 88 (0.1)	−379.250 81 (16.7)
7	−379.268 62 (4.2)	−379.273 76 (5.8)	−379.273 87 (2.2)
Proton affinities[c]	268.6	274.4	267.3

[a] In au. [b] In kcal mol^{-1}; difference between cited and most stable form. [c] In kcal mol^{-1}.

are almost the same for both compounds; only once do they differ by more than 1.5 kcal mol^{-1} between the phenol and its ether. This may be taken as indicating quite similar electronic effects of the hydroxy and methoxy substituents on support of charge at distant sites of the ring, and this similarity is in fact observed experimentally: the Hammett substituent constants for *m*-hydroxy and *m*-methoxy are the same within ±0.01 unit, and for the para substituents they differ by only 0.10 unit.[11] Further, the difference between the lowest protonated form of the meta isomer and the lowest protonated ortho isomer is remarkably constant for both the methylphenols and the methylanisoles, about 4.5 kcal mol^{-1}.

The proton affinities of the methylanisoles calculated by the STO-3G method are probably high, because the calculated value for benzene overestimates it by 25% using the best geometry.[12] The geometry here is not quite optimized for benzene, giving an energy 0.00358 au greater than the optimized form[3] However, it has been shown to be quite useful for predicting energy differences between proton affinities of substituted benzenes.[4] If the 25% excess found for benzene is constant, we estimate the proton affinities of these compounds to be: ortho, 214.9; meta, 219.5; para, 213.8 kcal mol^{-1}. In any case, the para form has the lowest proton affinity, and the ortho and meta isomers have proton affinities respectively 2 and 6 or 7 kcal mol^{-1} higher. That the meta form has the highest proton affinity is in accord, as we indicated earlier, with the simple ideas of substituent effects derived by organic chemists over the years. The proton affinities for the methylphenols with corrected geometries are: ortho, 239.3; meta, 243.7; para, 236.9 kcal mol^{-1}. When the estimated 25% excess is taken into account, these values become 191.4, 195.0, and 189.5 kcal mol^{-1}, respectively. Thus the calculations predict a difference of 20 to 25 kcal mol^{-1} in the proton affinities of the two classes. We suggest that this experiment be performed in a laboratory that is capable of it, for this difference is remarkably large; the difference between the proton affinities of water and methanol, for comparison, is only 17 kcal mol^{-1}.[13]

Charge Distributions

Figure 4 illustrates the total atomic populations for the neutral methylanisoles and Figure 5 the total atomic populations for the most stable protonated forms. These charge distributions can be compared with the corresponding methylphenols, because the small difference in geometry exhibited little effect on the atomic populations in general. It can be seen from Figure 4 that in all the methylanisoles the charge on oxygen is slightly more positive (by about 0.02 unit) than in the corresponding methylphenols. The only other significant

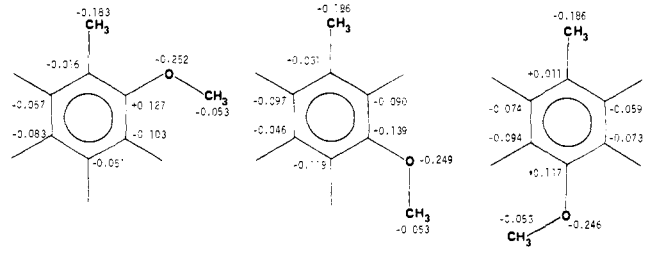


Figure 4. Total atomic populations for the neutral methylanisoles.

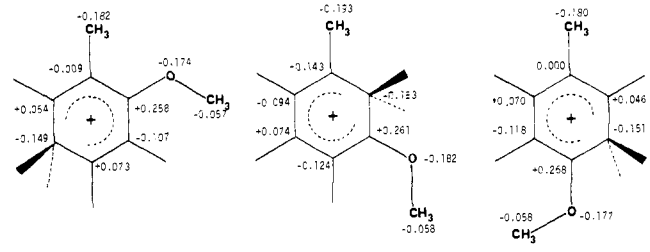


Figure 5. Total atomic populations for the most stable protonated methylanisoles.

change is a negative shift by 0.01 unit at the para carbon. From Figure 5, substitution of methyl for hydrogen in the methylphenols results in a slight positive shift on oxygen by about 0.02 unit. Obviously then, the methyl group is slightly more responsive to the demand of the positive charge in the molecules than the hydrogen it replaces, for upon protonation the withdrawal of electrons from the methyl group of the methylanisoles is greater than from the hydroxyl hydrogen that it replaces. This observation is generally in agreement with the observed effects upon acidity in the gas phase when hydrogen is replaced by methyl,[13] but the effect is a long-range one. Comparison of other changes in isomers upon protonation and with the protonated methylphenols yields no surprises. The carbon bearing the proton becomes more negative by about 0.06 electron; this behavior is very similar to the methylphenols, in which the carbon became 0.075 unit more negative upon protonation. The charge on the carbon of the methyl substituent is unchanged in both the methylphenols and their methyl ethers upon protonation. Finally, the carbons ortho and para to the site of protonation on the ring undergo a substantial depletion of electrons on the order of 0.1 or more units.

Again, the sum of the total atomic populations on the ring carbons is remarkably constant (−0.17 for the methylphenols; −0.18 for the methylanisoles). It is also constant for the most

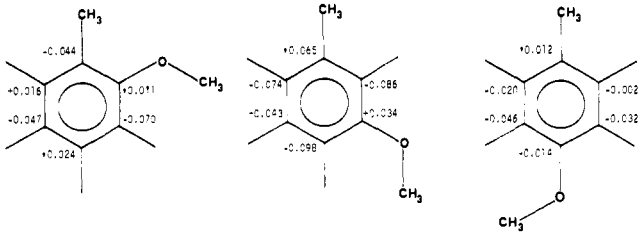


Figure 6. π orbital charges for the ring carbons of the neutral methylanisoles.

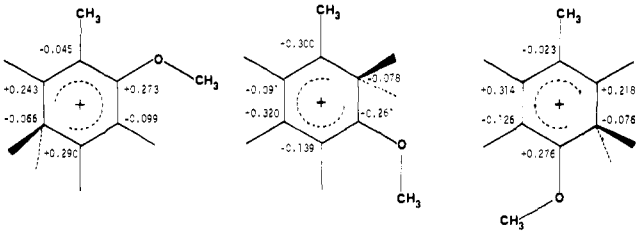


Figure 7. π orbital charges for the ring carbons of the most stable protonated methylanisoles.

stable protonated forms of the methylphenols (+0.13) and for the most stable protonated forms of the methylanisoles (+0.12). It is interesting to note that the neutral methylanisole with the least electron density in the ring is the para isomer, the one that has the greatest tendency to protonate at oxygen.

Figures 6 and 7 describe the π orbital populations in the uncharged and most stable protonated forms of the methylanisoles, respectively. There is only a slight accumulation of negative charge on the carbon protonated in both the ortho and para isomers and even a small positive shift in the meta isomer. In none of the isomers does the π orbital shift in charge at the ring-protonated carbon account for the total accumulation of negative charge there. The shift upon carbon protonation in the carbons ortho and para to the site of protonation is very large and positive, greater than the shift in total atomic population. One further observation is that upon protonation, the depletion of electrons from the ring carbon bound to oxygen is almost identical in both total and π orbital charges, indicating that a substantial proportion of the positive shift occurs in the π orbital. In these respects the effects of ring protonation of the methylanisoles are very similar to the effects in the methylphenols. Distinguishing features in the π system between the sets of neutrals are that there is more alternation of negative and positive charge in the π system of the *o*- and *m*-methylanisoles than in the corresponding methylphenols, while *p*-methylanisole has only one positively charged carbon in the π system. The protonated methylanisoles have fairly similar distributions of charge in the π system to the corresponding methylphenols.

Summary

To conclude, we observe that these calculations provide a basis for understanding the different experimental behavior of the methylanisoles in strong acids; they point up the similarities and differences of the methoxy and hydroxy substituents in aromatic rings; and they suggest comparable data for contrast with the experimental proton affinities when they can be determined.

Acknowledgment. The assistance of Mr. R. E. Martin with programs and the help and encouragement of the Director of the UNC Computation Center, Mr. James Batter, are gratefully acknowledged.

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