The Effect of the Methoxy Group on the Geometry of the Benzene Ring Supported by Crystal Structure Studies and *Ab Initio* Calculations. Crystal and Molecular Structure of 4-(4-Methoxyphenyl)-2,6-diphenylpyridine and 1-Methyl-4-(4-methoxyphenyl)-2,6-diphenylpyridinium Perchlorate.

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Abstract. *Crystal and molecular structures of 4-(4-methoxyphenyl)-2,6-diphenylpyridine (I) and 1-methyl-4-(4-methoxyphenyl)-2,6-diphenyl pyridinium perchlorate (II) are reported, with R=0.052 and 0.070, respectively. The lower precision of II is due to disorder of the perchlorate anion. A geometrical analysis of 8 p-substituted derivatives of anisole shows that the methoxy group interacts strongly with the ring via the resonance effect. Significant deformations of the exo-cyclic bond angles at MeO- substituted carbon atom are due to steric hindrance between ortho C-H and Me group. Ab initio calculations for anisole are in line with the observed planar conformation of these systems. The difference in energy between the planar and perpendicular conformers is 1.4 kcal/mole at the 6-31G* level. The intramolecular interactions between the -OMe group and $C_{ipso}-C_{ortho}H$ are explored through additional ab initio calculations. They induce more double character of $C_{ipso}-C_{ortho}$ bond, thereby causing one Kekule structure to be preferred.*

Introduction

The methoxy group, -OMe, is known as a moderate π-electron donating substituent with σ_R° value equal to -0.42.[1] Due to the resonance effect in p-methoxy derivatives of benzene, Scheme 1, one might expect systematic geometrical changes in both the methoxy group and the ring. The aim of this paper is to rationalize these effects, taking into account the geometries of p-methoxy derivatives of benzene (released from Cambridge Structural Database in October 93)[2,3,4] and the reported X-ray diffraction data for 4-(4-methoxyphenyl)-2,6-diphenylpyridine and 1-methyl-4-(4-methoxyphenyl)-2,6- diphenylpyridinium perchlorate obtained in our laboratory.
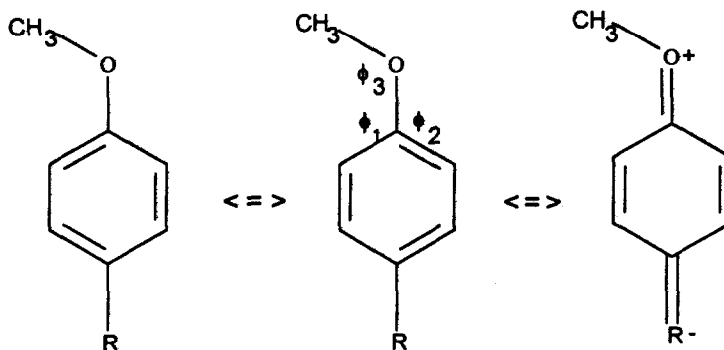
Scheme 1

Experimental

Melting points (uncorrected) were determined on a hot-stage microscope. The NMR spectra correspnding to approximately 0.15 M solutions in DMSO-d_6 were recorded at 20° C on a Varian Gemini spectrometer in FT mode at 50 MHz and 200 MHz for ^{1}H and ^{13}C, respectively. DMSO was used as an internal lock in the carbon spectra, and chemical shifts (δ, ppm) refer to its central peak (39.50 ppm). The spectral width was 10000Hz with 32 K data points giving a digital resolution of 0.6 Hz per point. The pulse width of 3.3 µs (90°) was used with a 0.970 s acquisition time. The precision of the carbon chemical shifts was estimated to be ±0.015 ppm. Proton-decoupled as well as proton DEPT technique[6] spectra were recorded. The proton chemical shifts referenced to the high frequency of an internal TMS are reliable to 0.005 ppm. The typical conditions were: spectral width 2.6 kHz, pulse width 11.3 µs, acquisition time 5.77 s for 32 measured data points.

4-(4-Methoxyphenyl)-2,6-diphenylpyridine (I) and 1-methyl-4-(4-methoxyphenyl)-2,6-diphenylpyridinium perchlorate (II) were obtained from 4-(4-methoxyphenyl)-2,6-diphenylpyrylium perchlorate according to ref 5

(I): m.p. 101.5-102.0°C (MeOH); ^{1}H NMR (δ ppm) 8.42 (dd, 4H, J = 1.5 and J = 7.8 Hz), 8.22 (s, 2H), 8.08 (d, 2H, J = 8.8 Hz), 7.67-7.54 (m, 6H), 7.20 (d, 2H, J = 8.8 Hz) and 3.92 (s, 3H); [13]NMR (δ ppm) 160.25, 156.33, 148.94, 138.84, 129.73, 128.93, 128.51, 128.46, 126.17, 115.77, 114.36 and 55.20.

(II): m.p. 206-211°C (MeOH polymorphic changes can be seen in the given temperature range); ^{1}H NMR (δ ppm) 8.49 (s, 2H), 8.39 (d, 2H, J = 8.9 Hz), 7.97-7.94 (m, 4H), 7.81-7.79 (m, 6H), 7.25 (d, 2H, J = 8.9 Hz), 3.98 (s, 3H) and 3.82 (s, 3H); ^{13}C NMR (δ ppm) 162.73, 156.03, 153.43, 133.03, 130.79, 130.38, 129.24, 128.97, 125.15, 123.72, 114.93, 55.54 and 44.98.

X-ray diffraction.

The X-ray measurements were made on a KUMA diffractometer with graphite monochromated CuKα radiation. The data were collected at room temperature using ω-2θ scan techniques. The intensity of the control reflections for both compounds varied by less than 5%, and a linear correction factor was applied to account for this effect. The data were also corrected for Lorentz and polarization effects, but no absorption correction was applied. All structures were solved by direct methods[7] and refined using SHELXL.[8] Non-hydrogen atoms were refined anisotropically and all H-atoms were placed in calculated positions and refined with isotropic thermal parameters. Atomic scattering factors were taken from the International Tables.[9] The details of X-ray measurements and structural computation and crystal data for 4-(4-methoxyphenyl)-2,6-diphenylpyridine (I) and 1-methyl-4-(4-methoxyphenyl)-2,6-diphenylpyridinium perchlorate (II) are given in Table 1. A perspective view of compounds (I) and (II) is shown in Fig.1, together with the atomic numbering scheme. Table 2 presents selected observed bond lengths and bond angles and dihedral angles for compounds (I) and (II).
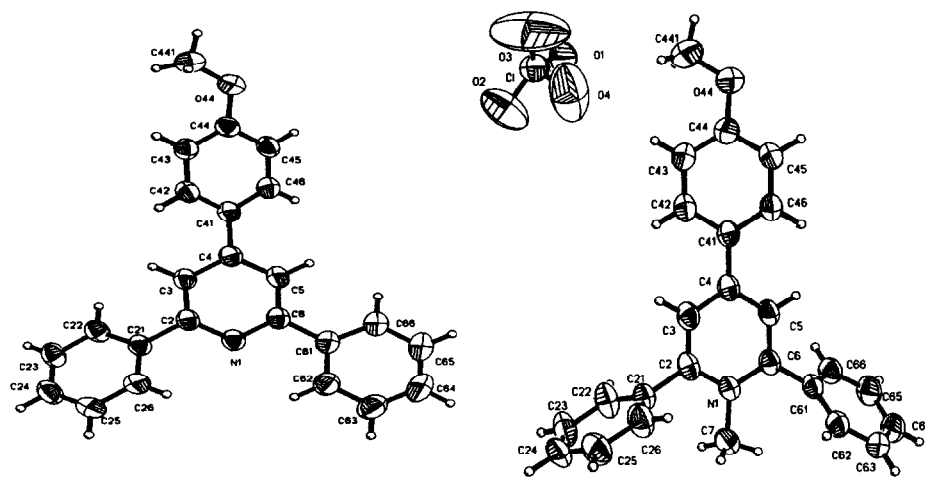

Fig.1. Perspective view of the compounds (I) and (II) with the labelling scheme used. All atoms are drawn with the same small arbitrary radius.

Table 1. Crystal data and structure refinement for 4-(4 -methoxyphenyl)-2,6-diphenylpyridine (I) and 1-methyl-4(4-methoxyphenyl-2,6-diphenylpyridinium perchlorate. (II).

Compound	I	II
Empirical formula	$C_{24}H_{19}NO$	$[C_{25}H_{22}NO]^+ClO_4^-$
Formula weight	337.40	451.90
Temperature	293(2)K	
Wavelength	1.54056A	
Crystal system	monoclinic	tetragonal
Space group	C2/c	I4₁/a
Unit cell dimensions	a=16.353(4)A	a=22.600(4)A
	b=10.111(2)A	b=22.600(4)A
	c=23.059(5)A	c=18.660(3)A
	$\alpha=90(2)^o$	$\alpha=90.00(2)^o$
	$\beta=108.04(2)^o$	$\beta=90.00(2)^o$
	$\gamma=90.00(2)^o$	$\gamma=90.00(2)^o$
Volume	$3625.3(14)A^3$	$9531(3)A^3$
Z	8	16
Density (calculated)	1.236Mg/m	1.260Mg/m
Absorption coefficient	$0.584mm^{-1}$	$1.711mm^{-1}$
F(000)	1424	1888
Crystal size	0.25x0.25x0.3mm	0.3x0.3x0.3mm
Theta range for data collection	$4.03to69.78^o$	$3.07to59.97^o$.
Index ranges	-17<=h>=17	0<=h<=24
	0<=k<=12	0<=k<=24
	0<=l<=24	0<=l<=20
Reflections collected	3325	3496
Independent reflections	3234	3311
	[R(int)=0.0265]	[R(int)=0.0133]
Refinement method	Full-matrix least-squareson F	
Data/restraints/ parameters	3217/0/254	3296/0/311
Goodness-of-fit on F	1.116	1.120
Final R indices [I>2sigma(I)]	R=0.0524 wR=0.1342	R=0.0703 wR=0.2020
R indices (all data)	R=0.0650 wR=0.1491	R=0.0995 wR=0.2386
Largest diff.peak and hole	$0.231and-0.413e.A^{-3}$	$0.411and-0.673e.A^{-3}$

Table 2 . Selected bond lengths [A] and angles [deg] for 4-(4-methoxyphenyl)-2,6-pyridine (I) and 1-methyl-4(4-methoxypheny)l-2,6-diphenylpyridinium perchlorate (II)

bond	I	II
N(1)-C(2)	1.346(2)	1.359(5)
N(1)-C(6)	1.351(2)	1.365(5)
N(1)-C(7)	-	1.481(5)
C(2)-C(3)	1.387(2)	1.365(6)
C(3)-C(4)	1.400(2)	1.399(5)
C(4)-C(5)	1.395(2)	1.390(5)
C(4)-C(41)	1.485(2)	1.466(5)
C(5)-C(6)	1.387(2)	1.364(5)
C(41)-C(46)	1.388(2)	1.389(5)
C(41)-C(42)	1.398(2)	1.394(5)
C(42)-C(43)	1.385(2)	1.376(6)
C(43)-C(44)	1.386(2)	1.385(6)
C(44)-O(44)	1.368(2)	1.359(5)
C(44)-C(45)	1.388(2)	1.393(6)
C(45)-C(46)	1.376(2)	1.375(6)
O(44)-C(441)	1.420(2)	1.409(6)

angles

|		
C(2)-N(1)-C(6)	117.79(1)	120.7(3)
C(2)-N(1)-C(7)	-	118.6(3)
C(6)-N(1)-C(7)	-	120.7(3)
N(1)-C(2)-C(3)	122.9(1)	120.0(3)
C(2)-C(3)-C(4)	119.8(1)	121.7(4)
C(5)-C(4)-C(3)	116.8(1)	115.6(4)
C(6)-C(5)-C(4)	120.5(1)	122.9(3)
C(5)-C(6)-N(1)	122.2(1)	119.0(3)
C(46)-C(41)-C(42)	117.3(1)	117.2(4)
C(46)-C(41)-C(4)	120.5(1)	121.8(3)
C(42)-C(41)-C(4)	122.2(1)	121.0(3)
C(43)-C(42)-C(41)	122.0(1)	122.0(4)
C(42)-C(43)-C(44)	119.6(1)	119.7(4)
O(44)-C(44)-C(43)	124.6(1)	124.9(4)
O(44)-C(44)-C(45)	116.2(1)	115.6(3)
C(43)-C(44)-C(45)	119.3(1)	119.5(4)
C(46)-C(45)-C(44)	120.5(1)	119.7(4)
C(45)-C(46)-C(41)	121.3(1)	121.9(4)
C(44)-O(44)-C(441)	117.4(1)	118.0(4)

Calculational details.

Ab initio calculations utilized Gaussian 92[10] and were carried out on the CONVEX C3800 supercomputer at the University of London Computer Centre. The standard 6-31G* basis set of Pople   et al was used[11], and geometry optimization employed the Berny Algorithm with the condition that the maximum force on any   nucleus   should   not   exceed 2×10^{-4}a.u. The advantages of the ab initio approach for this work are two-fold: (i) it may give independent

confirmation of the results based on crystallographic data, where intermolecular interactions may also be important, (ii) it allows us to study hypothetical structures, such as the one where the methoxy group is perpendicular to the ring.

Results and discussion.

Analysis of X-ray structural data.

The methoxy group as a moderate π-electron donating group is expected to interact with the π-electron system of Ph-R in the way presented in Scheme 1. Hence one may expect a variaton of the quinoid structure contribution dependent on the nature of the p-substituent R, Table 3. It results from Scheme 1 that an increase of the quinoid structure contribution should be accompanied by the shortening of the C_{ring}-O and lengthening of the of O-CH$_3$ interatomic distances. The resonance effect between the methoxy-group and the ring may be proved by relating statistically independent quantities: the changes in geometry of the ring with the C_{ring}-O interatomic distances. Since the HOSE-model[12] provides an estimate of the canonical structure contributions from experimental bond lengths of π-electron systems, the CC bond lengths of the ring were used to calculate the relative weights of Q and B_1 and B_2 "canonical structures" as depicted in Scheme 2. We should stress that these are fragments of the full canonical structures of Scheme 1, taking into account only carbon atoms of the aromatic ring.

$$B_1 \quad <=> \quad B_2 \quad <=> \quad Q$$
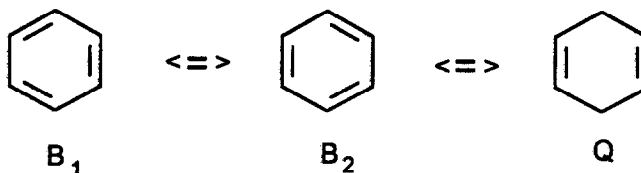
Scheme 2

Exocyclic CC-bonds were not used in these calculations. Fig 2 presents the scatter graph of %Q vs C_{ring}-O bond lengths which supports the above presented interpretation: an increase of bond lengths C_{ring}-O is accompanied by a decrease of %Q. Table 3 presents the relevant data.
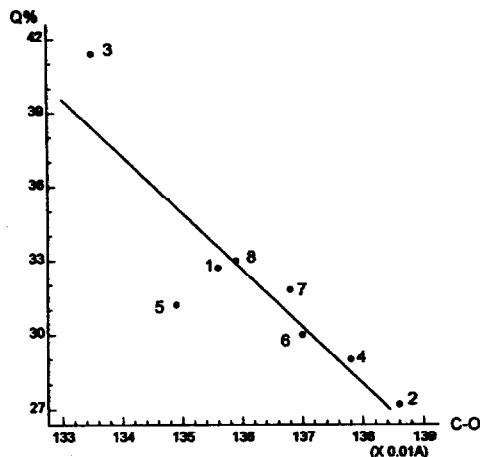
Fig 2. The relationship between the quinoid structure contribution Q and the C_{ring}-O interatomic distance for 8 p-substituted derivatives of anisole. Labelling scheme as in Table 3.

TABLE 3. Geometric parameters and quinoid structure contributions for nine p-methoxy derivatives of benzene.

R	$R_{C-O}(A)$	$R_{O-Me}(A)$	Q%	$\varphi_1(^o)$	$\varphi_2(^o)$	Ref.
1.-COOH	1.356	1.435	32.7	124.3	115.5	13
2.-NH$_2$	1.386	1.420	27.2	124.2	116.3	17
3.-N=O	1.335	1.444	41.4	125.4	115.5	18
4.-N=CHPhOH	1.378	1.420	29.0	124.5	115.4	19
5.-(COOCH$_2$C C-)$_2$	1.349	1.419	31.2	125.2	115.4	20
6.-COOCH$_2$CH$_2$NHMe$_2^+$Cl$^-$	1.370	1.423	30.0	126.1	113.7	21
7.-Py (I of Fig.1.)	1.368	1.420	31.8	124.6	116.2	this work
8.-Py$^+$ (II of Fig.1)	1.359	1.409	33.0	124.9	115.6	this work
9.NHCOCH*	1.393	1.441	31.2	124.3	116.0	22

*   these data [22] were not taken into account, due to relatively low
er precision of the   measurement (photographic methods) and the plate form of the crystal.

Another interesting feature of this family of compounds is that the exocyclic bond angles at C44 deviate considerably from 120°. The   differences (φ_1-φ_2) are in the range 7.2   -11.5^o . Moreover, the greater angle is always at the same side of COMe, shown in Scheme 1. It was already mentioned[13] that it might be caused by steric hindrance between the CH$_3$ group and the hydrogen   C43H bond. This effect was observed too for the calculated geometry of anisole by ab $initio$ methods using STO-3G[14] and 6-31G[15] basis sets. From the crystallographic point of view this effect should be associated with short interatomic contacts C43-H...Me-, and

indeed it is. In molecules I and II of Fig.1 these distances are 2.50 and 2.52 A respectively, i.e. considerably shorter than the sum of the Van der Waals radii of H (1.20 A) and C (1.68 A)[16] i.e. 2.88 A. Therefore it may be accepted that steric interactions between the methyl group and ortho C-H hydrogen atom explains the deformation of angles at C44.

Ab initio 6-31G* calculations for anisole.

Undoubtedly the observed distortion of the bond angle φ_1 from the "ideal" value of 120° needs energy. It may be taken either from packing forces the crystal, lattice or from intramolecular interactions between the π-electron system of the phenyl ring. The first case may be excluded, since in the gas phase anisole is planar[23]. In order to estimate the strength of the intramolecular interactions between methoxy group and the ring, we have carried out 6-31G* calculations with optimization of the geometry, for two conformers: the planar one (PL) which is of the lowest energy and the perpendicular one (PE) for which the only constraint is perpendicularity of methoxy group with respect to the ring plane. The PL conformer was found to be more stable by 1.39 kcal mol^{-1} in spite of the deformation of φ_1. The *ab initio* optimized value was 124.9° which may be compared to the range of φ_1 values in Table 3 ($124.2\text{-}126.1^\circ$). It means that the overall effect due to conjugation between the methoxy group and the ring must have been somewhat greater. All geometry details for both conformers are given in Table 4.

Table 4. 6-31G* calculated geometry. Labelling scheme as in Fig.1.

	PE	PL*	PL with C44O44C441 angle114.8	PL with C44O44C441 angle109.8
angle				
C44O44C441**	115.5	119.8	114.8	109.8
bond			(constraint)	(constraint)
C43-C44	1.386	1.386	1.386	1.387
C42-C43	1.385	1.391	1.386	1.377
C41-C42	1.386	1.380	1.386	1.377
C41-C46	1.386	1.391	1.391	1.391
C45-C46	1.385	1.378	1.377	1.376
C44-C45	1.386	1.393	1.395	1.397
C44-O44	1.363	1.350	1.357	1.367
O44-C441	1.405	1.398	1.403	1.410
%B$_1$***	50	52.6	58.0	60.8
HOMA	0.999	0.991	0.990	0.984
total energy (Hartree)	-344.581029	-344.583262	-344.582004	-344.577835

*   equilibrium geometry, optimized.

**   experimental value (gas phase electron diffraction [23]) is 120.9°

***   see Scheme 2, the double bond in B$_1$ is 'under' the bent OCH$_3$ group and reflects the canonical structure on the left side of Scheme 1.

Additional support for the conjugation comes out from the comparison of Mulliken charges at oxygen atoms in PL and PE conformers, equal to -0.652 and -0.664, respectively. The difference is slight but important since we take here into account net charges composed of σ- and π-electron contributions. Thus the mesomeric effect may be masked by σ-electron compensation.

Looking at the geometry (bond lengths) of the PE and PL conformers gathered in Table 4, it is evident that the PE form has much more equalized CC bond lengths in the ring than the PL form. When the contributions of the two Kekule structures are calculated by use of the HOSE model for these geometries[12], it is apparent that for PE they are equal each other, whereas for PL they are 47.4 and 52.6%. This observation suggests that the bent C44-O44-Me group interacting with C44-C43 and C43H induces shortening of the C44-C43 bond. Therefore we have carried out two further calculations for PL conformers with optimization of geometry but with the constraint that the C44-O44-C441 angle is 114.8 and 109.8°, i.e. 5° and 10° less than in the PL conformer. In this way we forced the π-electron system to interact more strongly with this bent methoxy group. The results obtained appear in Table 4. They seem to verify our hypothesis: the deformation of the ring towards one particular Kekule structure increases with the strength of this interaction (i.e. smaller C44-O44-C441 angle). The contribution of the Kekule structure to the double bond C44-C43 becomes stronger with an increase of these interactions, increasing from 50% (PE form, no such interactions) to 52.,6% for PL and to 58.0% and 60.8% for PL with the C44-O44-C441 angles 114.8° and 109.8°, respectively. This is associated with a decrease of the aromatic character estimated by the HOMA-index[24] (Table 4).

Conclusions:

(1) As a result of steric hindrance between CH_3 of methoxy group and C43-H of the ring there is an increase of the C43-C44-C44 bond angle and

(2) the C44-C43 bond indicates a stronger double bond character that the C44-C45 bond, which may have implications for preferred sites of nucleophilic reactivity.

Acknowledgements

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