

Substituent Effects on the Geometry of the Pyridine Ring in 1-Methyl-4-(4-R-phenyl)-2,6-diphenylpyridinium Perchlorates

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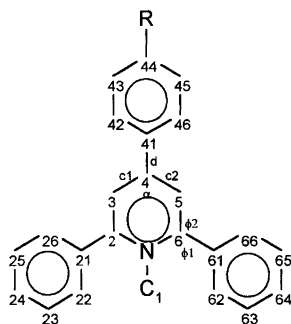
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The crystal and molecular structure of the derivatives of 1-methyl-4-(4-R-phenyl)-2,6-diphenylpyridinium perchlorates, [R = H, F, Cl, NO₂, N(CH₃)₂] have been solved by X-ray diffraction techniques at room temperature with Cu K α radiation. Deformations of geometry in the pyridine ring are mesomeric in nature. They depend on the kind of substituent and may be explained by use of the modified Bent–Walsh rule. The charged N-atom in N⁺–H and N⁺–M derivatives of pyridine has an enhanced electronegativity which is demonstrated by changes in exocyclic bond angles at the *ortho* carbon atoms in the ring. The mean angles for 12 entries (CSD release April 1994) of N⁺–H derivatives are 118.1° and 123.2°, respectively, as expected from the Bent–Walsh rule. The title compounds do not exhibit these deformations, mean values for the above-mentioned angles being 119.9° and 120.5°. This effect is due to steric interactions between the Me group in N⁺ Me and neighbouring phenyl moieties which act against the electronegativity effect at C2 and C6 positions.

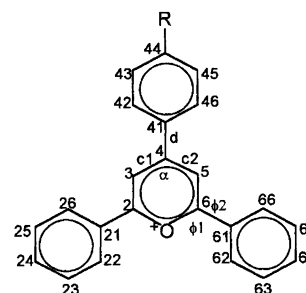
Among the numerous classes of heterocyclic cations the *N*-substituted pyridinium salts have been extensively studied from synthetic, physicochemical and biological points of view.¹ Thus, aryl-substituted pyridinium salts are distinguished by the variety of their transformations into compounds that are normally hard to obtain.^{2,3} In par-

ticular, replacement of the amino group of primary alkyl and (hetero) aryl amines by a nucleophile *via* the corresponding 2,4,6-triphenylpyridinium cations has been used in the conversion of amines into halides, alcohols and esters.² The studies of mechanistic problems of those processes have been carried out by Katritzky and co-workers.^{4,5}

Some aryl-substituted pyridinium salts are interesting examples of donor–acceptor dyes.⁶ Others have been used in the synthesis of dyes showing improved photo-



Scheme 1.



Scheme 2.

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Table 1. Crystal data and structure refinement for 1-methyl-4-(4-R-phenyl)-2,6-diphenylpyridinium perchlorate.

R	H	Cl	F	NO ₂	N(CH ₃) ₂
Empirical formula	[C ₂₄ H ₂₀ N] ⁺ [ClO ₄] ⁻	[C ₂₄ H ₁₉ NCI] ⁺ [ClO ₄] ⁻	[C ₂₄ H ₁₉ NF] ⁺ [ClO ₄] ⁻	[C ₂₄ H ₁₉ NO ₂] ⁺ [ClO ₄] ⁻	[C ₂₆ H ₂₅ N ₂] ⁺ [ClO ₄] ⁻
Formula weight	421.86	456.30	439.85	466.88	464.95
Temperature		293(2) K			293(2) K
Wavelength	1.54178 Å	1.54178 Å			1.54178 Å
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>Pbca</i>	<i>P2(1)/n</i>	<i>P2(1)/n</i>	<i>P2(1)/n</i>	<i>P2(1)/n</i>
Unit cell dimensions	<i>a</i> = 15.289(3) Å <i>b</i> = 15.602(4) Å <i>c</i> = 17.960(3) Å	<i>a</i> = 13.120(4) Å <i>b</i> = 11.853(2) Å <i>c</i> = 14.182(5) Å β = 103.35(3)° 2145.9(11) Å ³	<i>a</i> = 12.750(5) Å <i>b</i> = 11.775(2) Å <i>c</i> = 14.290(5) Å β = 102.40(3)° 2095.3(12) Å ³	<i>a</i> = 13.397(3) Å <i>b</i> = 11.833(2) Å <i>c</i> = 14.340(3) Å β = 105.83(3)° 2187(8) Å ³	<i>a</i> = 7.979(4) Å <i>b</i> = 17.892(8) Å <i>c</i> = 16.954(8) Å β = 97.52(4)° 2400(12) Å ³
<i>V</i> /Å ³	4284(12)	4	4	4	4
<i>Z</i>	8	4	4	4	4
Density (calculated)/Mg m ⁻³	1.308	1.412	1.394	1.418	1.287
Absorption coefficient/mm ⁻¹	1.830	2.990	1.966	1.935	1.693
<i>F</i> (000)	1760	944	912	968	976
Crystal size/mm	0.25 × 0.25 × 0.25	0.25 × 0.25 × 0.30	0.25 × 0.25 × 0.25	0.30 × 0.26 × 0.28	0.28 × 0.25 × 0.25
θ range for data collection/°	<i>h</i> < = 17 <i>k</i> < = 17 <i>l</i> < = 13	4.74–70.16 <i>h</i> < = 15 <i>k</i> < = 13 <i>l</i> < = 16	4.74–70.16 <i>h</i> < = 15 <i>k</i> < = 14 <i>l</i> < = 16	4.74–70.16 <i>h</i> < = 15 <i>k</i> < = 13 <i>l</i> < = 16	4.74–70.16 <i>h</i> < = 9 <i>k</i> < = 20 <i>l</i> < = 19
Index ranges		Full-matrix least-squares on <i>F</i> ²			Full-matrix least-squares on <i>F</i> ²
Refinement method		3237/0/299	3689/0/299	3553/0/314	3749/0/341
Data/restraints/parameters	2915/0/309	<i>R</i> 1 = 0.0832, <i>wR</i> 2 = 0.2177	<i>R</i> 1 = 0.0679, <i>wR</i> 2 = 0.1775	<i>R</i> 1 = 0.0760, <i>wR</i> 2 = 0.1983	<i>R</i> 1 = 0.0753, <i>wR</i> 2 = 0.2069
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0586, <i>wR</i> 2 = 0.1565	<i>R</i> 1 = 0.0832, <i>wR</i> 2 = 0.2177	<i>R</i> 1 = 0.0679, <i>wR</i> 2 = 0.1775	<i>R</i> 1 = 0.0760, <i>wR</i> 2 = 0.1983	<i>R</i> 1 = 0.0753, <i>wR</i> 2 = 0.2069
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0886, <i>wR</i> 2 = 0.1902	<i>R</i> 1 = 0.0938, <i>wR</i> 2 = 0.2576	<i>R</i> 1 = 0.0866, <i>wR</i> 2 = 0.2020	<i>R</i> 1 = 0.1027, <i>wR</i> 2 = 0.2385	<i>R</i> 1 = 0.1178, <i>wR</i> 2 = 0.2655
Largest diff. peak and hole/e Å ⁻³	0.321 and -0.502	0.745 and -0.963	0.430 and -0.735	0.611 and -0.547	0.368 and -0.571

Table 2 Geometric parameters of the 1-methyl-4-(4-R-phenyl)-2,6-diphenylpyridinium perchlorates.

R	H	Cl	F	NO ₂	N(CH ₃)
Selected bond lengths (Å)					
N1–C1	1.475(4)	1.483(4)	1.485(3)	1.493(4)	1.476(5)
N1–C2	1.358(4)	1.367(4)	1.360(3)	1.354(4)	1.367(4)
N1–C6	1.380(3)	1.372(4)	1.373(3)	1.367(4)	1.364(5)
C2–C3	1.367(4)	1.381(5)	1.376(3)	1.387(4)	1.400(5)
C3–C4	1.402(4)	1.385(4)	1.400(4)	1.396(4)	1.400(5)
C4–C5	1.390(4)	1.395(4)	1.386(4)	1.391(4)	1.403(5)
C5–C6	1.371(4)	1.369(4)	1.376(3)	1.380(4)	1.355(5)
C2–C21	1.490(3)	1.486(4)	1.490(3)	1.485(5)	1.488(5)
C4–C41	1.472(4)	1.475(4)	1.477(3)	1.485(5)	1.460(5)
C41–C42	1.382(5)	1.399(4)	1.387(4)	1.394(5)	1.389(5)
C41–C46	1.404(4)	1.392(4)	1.399(4)	1.395(4)	1.395(6)
C42–C43	1.373(5)	1.371(4)	1.389(4)	1.383(5)	1.372(5)
C43–C44	1.387(5)	1.385(5)	1.357(5)	1.375(5)	1.397(6)
C44–C45	1.360(6)	1.378(5)	1.361(5)	1.377(5)	1.388(6)
C45–C46	1.388(5)	1.381(5)	1.386(4)	1.377(4)	1.360(6)
C6–C61	1.477(4)	1.479(4)	1.481(3)	1.483(4)	1.483(5)
C44–Cl	—	1.741(3)	—	—	—
C44–F	—	—	1.362(3)	—	—
C44–N2	—	—	—	1.478(5)	1.372(5)
N2–O1	—	—	—	1.226(5)	—
N2–O2	—	—	—	1.213(5)	—
N2–C441	—	—	—	—	1.456(7)
N2–C442	—	—	—	—	1.454(7)
Selected bond angles (°)					
C1–N1–C2	119.7(2)	120.8(2)	119.2(2)	120.5(3)	119.8(3)
C1–N1–C6	119.8(2)	118.6(3)	120.6(2)	121.1(3)	119.9(3)
C2–N1–C6	120.2(2)	120.4(3)	120.1(2)	118.2(3)	120.1(3)
C3–C2–N1	120.2(3)	119.6(3)	120.4(2)	119.7(3)	119.9(3)
C4–C5–C2	122.0(3)	121.1(3)	121.5(2)	121.3(3)	122.4(3)
C5–C4–C3	115.8(3)	116.1(3)	115.9(2)	116.8(3)	114.9(3)
C6–C5–C4	122.4(3)	122.1(3)	122.8(3)	121.8(2)	122.8(3)
N1–C6–C5	119.3(3)	119.5(3)	119.2(2)	119.3(3)	119.9(3)
N1–C2–C21	119.3(3)	120.7(3)	119.0(2)	121.2(3)	118.7(4)
C2–C2–C21	120.5(3)	119.6(3)	120.6(2)	119.1(3)	121.4(3)
C2–C21–C22	122.2(3)	119.6(3)	120.6(2)	119.0(3)	121.5(4)
C2–C21–C26	119.0(3)	119.2(3)	119.0(2)	120.8(3)	119.0(4)
C3–C4–C41	122.9(3)	121.5(3)	121.7(2)	121.2(3)	122.9(3)
C5–C4–C46	121.3(3)	122.2(3)	122.3(2)	121.2(3)	121.1(3)
C4–C41–C42	121.4(3)	120.1(3)	122.0(3)	119.7(4)	122.5(3)
C4–C41–C46	120.9(3)	121.8(3)	119.6(2)	121.5(3)	120.0(3)
C42–C41–C46	117.7(3)	118.0(3)	118.4(2)	118.6(3)	115.5(3)
C43–C42–C41	122.4(3)	121.5(3)	120.9(3)	120.8(3)	122.1(4)
C44–C43–C42	119.0(3)	118.9(3)	118.6(3)	118.5(3)	121.6(4)
C45–C44–C43	120.1(4)	121.5(3)	122.9(3)	122.6(3)	116.6(4)
C46–C45–C44	121.0(3)	118.9(3)	118.7(3)	118.3(3)	121.2(4)
C41–C46–C45	119.8(4)	121.3(3)	120.5(3)	121.2(3)	123.1(4)
N1–C6–C61	120.3(3)	121.3(3)	120.8(2)	121.0(3)	119.8(3)
C5–C6–C61	120.4(3)	119.1(3)	119.9(2)	119.7(3)	120.3(3)
C6–C61–C62	121.8(3)	119.8(3)	119.1(2)	120.9(3)	120.9(3)
C6–C61–C66	119.2(3)	120.7(3)	121.5(2)	119.5(3)	120.2(3)
C43–C44–Cl	—	120.3(3)	—	—	—
C45–C44–Cl	—	118.6(2)	—	—	—
C43–C44–F	—	—	119.0(3)	—	—
C45–C44–F	—	—	118.1(3)	—	—
C44–N2–O1	—	—	—	119.1(4)	—
C44–N2–O2	—	—	—	116.4(4)	—
O1–C44–O2	—	—	—	124.4(4)	—
C44–N2–C441	—	—	—	—	120.5(4)
C44–N2–C442	—	—	—	—	120.7(4)
C441–N2–C442	—	—	—	—	118.7(4)

Table 2 Continued

R	H	Cl	F	NO ₂	N(CH ₃)
Selected torsion angles (°)					
N1–C2–C21–C22	–128.7(3)	129.4(3)	114.7(3)	127.3(3)	–110.2(4)
C3–C2–C21–C22	52.1(4)	–52.4(4)	–67.5(3)	–54.8(4)	69.4(5)
N1–C2–C21–C26	56.4(4)	–56.2(4)	–67.3(3)	–55.5(4)	72.6(5)
C3–C2–C21–C26	–122.8(3)	121.9(3)	110.4(3)	122.4(3)	–107.7(4)
C3–C4–C41–C42	–25.1(4)	161.3(3)	19.9(3)	–20.2(4)	–20.1(6)
C5–C4–C41–C42	154.8(3)	–23.3(4)	–163.8(3)	154.5(3)	161.3(5)
C3–C4–C41–C46	156.7(3)	–20.7(4)	–157.2(3)	163.8(3)	160.3(5)
C5–C4–C41–C46	–23.4(4)	154.6(3)	19.1(3)	–21.0(4)	–18.3(6)
N1–C6–C61–C62	128.9(3)	–115.0(3)	–128.6(3)	65.2(4)	117.5(4)
C5–C6–C61–C62	–50.8(4)	66.8(4)	52.7(3)	–112.5(3)	–63.8(5)
N1–C6–C61–C66	–57.6(4)	65.8(4)	65.7(3)	–117.1(3)	–64.7(5)
C5–C6–C61–C66	122.8(3)	–112.4(3)	–121.9(3)	65.2(4)	117.5(4)
Closest contacts (°) between H (from CH ₃ group) and <i>ortho</i> H atoms from neighbouring phenyl groups					
H13–H26	2.134(6)				
H11–H66	2.355(6)	2.589(5)	2.317(4)		
H12–H22	—	2.144(5)	2.373(4)		
H11–H26	—	—	—	2.666(6)	2.660(7)
H12–H66	—	—	—	2.316(7)	2.316(6)

stability.⁷ It should be mentioned that some of 1-aryl-2,4,6-triaryl-substituted pyridinium salts are the most typical betaine dyes which show intense negative solvatochromic properties.⁸

1-Alkyl-2,4,6-triaryl-substituted pyridinium salts are convenient model compounds for the study of several photoinduced processes, such as fluorescence with an anomalous Stokes shift (ASS), intramolecular charge transfer (ICT) and photochemical reactions.^{9–12}

Intramolecular interactions between the R substituent and the pyridine ring in the title series (Scheme 1) are similar to the series of 4-(4-R-phenyl)-2,6-diphenylpyrylium salts (Scheme 2). Changes of geometry in pyrylium salts exhibited regularities which could be described by linear dependences of aromaticity of both central rings on the nature of the substituent.^{13–15} A considerable deformation of bond angles at C2 and C6 was attributed to a strong electronegativity effect of the oxygen atom in the ring and enhanced by its positive charge.¹⁶ The angular deformations in the pyrylium ring were found to be regularly dependent on the nature of the 4-R substituent.¹⁷

The aim of this work was to determine the crystal and molecular structures of the title compounds and to study how far the above mentioned regularities observed for pyrylium salts are still applicable to similarly substituted derivatives of pyridinium salts taking into account the lesser electron-accepting power of the pyridine ring as a substituent and the possibility of steric interactions in the neighbourhood of the N⁺–Me fragment.

Experimental

The X-ray measurements of five crystals (Scheme 1) were made on a KUMA diffractometer with graphite mono-

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1-methyl-2,4,6-triphenylpyridinium perchlorate. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
N(1)	1540(1)	5992(1)	12677(1)	50(1)
C(1)	1866(2)	6533(2)	12063(2)	66(1)
C(2)	1359(2)	6350(2)	13348(2)	52(1)
C(21)	1342(2)	7300(2)	13436(2)	55(1)
C(22)	1823(2)	7670(2)	14003(2)	71(1)
C(23)	1774(2)	8543(2)	14134(3)	86(1)
C(24)	1248(3)	9052(2)	13698(3)	85(1)
C(25)	769(2)	8694(2)	13144(2)	79(1)
C(26)	809(2)	7819(2)	13008(2)	66(1)
C(3)	1178(2)	5841(2)	13948(2)	55(1)
C(4)	1180(2)	4944(2)	13899(2)	53(1)
C(41)	1034(2)	4405(2)	14560(2)	55(1)
C(42)	1219(2)	4701(2)	15268(2)	66(1)
C(43)	1133(2)	4195(3)	15889(3)	78(1)
C(44)	848(2)	3356(3)	15806(3)	78(1)
C(45)	641(2)	3051(2)	15119(3)	81(1)
C(46)	724(2)	3563(2)	14490(2)	67(1)
C(5)	1328(2)	4607(2)	13194(2)	56(1)
C(6)	1499(2)	5114(2)	12587(2)	51(1)
C(61)	1642(2)	4725(2)	11848(2)	55(1)
C(62)	2245(2)	4060(2)	11776(2)	68(1)
C(63)	2329(3)	3644(2)	11096(3)	85(1)
C(64)	1826(3)	3868(2)	10499(3)	80(1)
C(65)	1224(2)	4521(2)	10573(2)	78(1)
C(66)	1131(2)	4945(2)	11235(2)	67(1)
Cl	945(1)	3468(1)	8176(1)	63(1)
O(1)	1188(2)	2670(2)	7843(2)	94(1)
O(2)	539(3)	4012(2)	7662(2)	124(1)
O(3)	1648(3)	3801(3)	8569(4)	97(2)
O(4)	235(3)	3281(4)	8667(4)	111(2)
O(5)	1672(10)	4063(11)	7954(14)	150(8)
O(6)	789(20)	3525(13)	8914(9)	157(11)

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1-methyl-4-(4-chlorophenyl)-2,6-diphenylpyridinium perchlorate. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
N(1)	-3377(2)	3589(2)	3515(2)	36(1)
C(1)	-2668(3)	4351(3)	3136(3)	48(1)
C(2)	-3406(3)	3611(2)	4465(2)	36(1)
C(21)	-2622(3)	4270(3)	5177(2)	42(1)
C(22)	-1550(3)	4083(3)	5294(3)	55(1)
C(23)	-841(4)	4667(4)	6005(3)	67(1)
C(24)	-1194(4)	5429(4)	6603(4)	72(1)
C(25)	-2235(4)	5591(3)	6495(3)	66(1)
C(26)	-2967(3)	5017(3)	5796(2)	48(1)
C(3)	-4154(3)	2988(3)	4779(2)	39(1)
C(4)	-4871(2)	2314(2)	4155(2)	35(1)
C(41)	-5609(2)	1581(3)	4513(2)	36(1)
C(42)	-6515(3)	1154(3)	3894(2)	45(1)
C(43)	-7173(3)	432(3)	4223(2)	47(1)
C(44)	-6930(3)	125(3)	5191(3)	43(1)
C(2)	-7755(1)	-782(1)	5634(1)	61(1)
C(45)	-6054(3)	541(3)	5828(2)	42(1)
C(46)	-5399(3)	1266(3)	5485(2)	40(1)
C(5)	-4801(2)	2308(3)	3189(2)	38(1)
C(6)	-4059(2)	2920(2)	2873(2)	35(1)
C(61)	-3956(2)	2849(2)	1858(2)	35(1)
C(62)	-4742(3)	3254(3)	1107(2)	45(1)
C(63)	-4638(3)	3179(3)	157(2)	48(1)
C(64)	-3761(3)	2685(3)	-43(2)	45(1)
C(65)	-2981(3)	2270(3)	699(2)	45(1)
C(66)	-3064(3)	2357(3)	1650(2)	43(1)
Cl(1)	65(1)	1264(1)	2251(1)	54(1)
O(1)	973(2)	1906(3)	2242(2)	67(1)
O(2)	-498(2)	1027(3)	1285(2)	67(1)
O(3)	377(5)	251(5)	2733(4)	163(3)
O(4)	-571(3)	1888(7)	2735(3)	161(3)

chromated Cu $K\alpha$ radiation. The data were collected at room temperature using the ω - 2θ scan technique. The intensity of control reflections for the five 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 methods¹⁸ and refined using SHELXL.¹⁹ Non-hydrogen atoms were refined anisotropically, whereas all H-atoms were placed in calculated positions and their thermal parameters were refined isotropically. Atomic scattering factors were taken from the *International Tables*.²⁰ The details of X-ray measurements and structural computation, and crystal data for five 1-methyl-4-aryl-2,6-diphenylpyridinium perchlorates are given in Table 1. Table 2 presents selected bond lengths and bond angles in the compounds: 1-methyl-2,4,6-triphenylpyridinium perchlorate (**1**), 1-methyl-4-(4-chlorophenyl)-2,6-diphenylpyridine perchlorate (**2**), 1-methyl-4-(4-fluorophenyl)-2,6-diphenylpyridinium perchlorate (**3**), 1-methyl-4-(4-nitrophenyl)-2,6-diphenylpyridinium perchlorate (**4**) and 1-methyl-4-(4-dimethylaminophenyl)-2,6-diphenylpyridinium perchlorate (**5**) and their equivalent

Table 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1-methyl-4-(4-fluorophenyl)-2,6-diphenylpyridinium perchlorate. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
N(1)	3429(2)	1423(2)	6526(2)	41(1)
C(1)	2688(2)	661(2)	6901(2)	52(1)
C(2)	4139(2)	2071(2)	7150(2)	42(1)
C(21)	4052(2)	2116(2)	8172(2)	42(1)
C(22)	3165(2)	2633(2)	8415(2)	48(1)
C(23)	3109(2)	2711(2)	9372(2)	53(1)
C(24)	3907(2)	2263(2)	10071(2)	53(1)
C(25)	4786(2)	1739(2)	9835(2)	55(1)
C(26)	4864(2)	1679(2)	8881(2)	52(1)
C(3)	4901(2)	2705(2)	6834(2)	45(1)
C(4)	4957(2)	2726(2)	5866(2)	43(1)
C(41)	5714(2)	3477(2)	5512(2)	45(1)
C(42)	6612(2)	3932(3)	6119(2)	57(1)
C(43)	7270(2)	4700(3)	5781(3)	68(1)
C(44)	7025(2)	4984(3)	4839(3)	65(1)
F(1)	7659(2)	5746(2)	4502(2)	98(1)
C(45)	6167(2)	4545(2)	4209(2)	58(1)
C(46)	5503(2)	3785(2)	4544(2)	49(1)
C(5)	4129(2)	2050(2)	5258(2)	45(1)
C(6)	3455(2)	1415(2)	5570(2)	42(1)
C(61)	2660(2)	754(2)	4873(2)	45(1)
C(62)	3021(2)	8(2)	4255(2)	53(1)
C(63)	2291(3)	-562(3)	3560(2)	67(1)
C(64)	1205(3)	-392(3)	3465(2)	72(1)
C(65)	846(3)	355(3)	4068(3)	71(1)
C(66)	1565(2)	927(2)	4771(2)	58(1)
Cl(1)	4981(1)	1369(1)	2771(1)	59(1)
O(1)	5569(2)	1124(2)	3713(2)	71(1)
O(2)	4043(2)	1993(2)	2807(2)	74(1)
O(3)	5620(3)	2038(5)	2284(2)	165(2)
O(4)	4684(4)	359(3)	2284(3)	176(2)

temperature factors for non-hydrogen atoms are given in Tables 3–7. All compounds studied were obtained according to Ref. 21.

Results and discussion

The title compounds form a convenient sample for studying the substituent effect on the geometry of the transmitting benzene ring with the C41–C46 atoms, the central bond C4–C41 (d), and the pyridine ring (Scheme 1). The pyridine ring is positively charged due to methylation at the nitrogen ring atom and acts as an electron-accepting moiety. One might expect that this ring would be affected by electron-donating properties of the substituents at the C44 atom of the 4-R-substituted benzene ring and ring geometries might be a good indicator of those interactions. Thus $R = \text{NMe}_2$, OMe ,²⁷ Cl , F and NO_2 , is a good range of substituents for a study of these effects. Apart from the simple structural parameters like bond angles, bond lengths, etc., there are also complex model quantities such as HOMA-values,²² which describe the aromatic character of the pyridine ring and the 4-R substituent.

Table 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1-methyl-4-(4-nitrophenyl)-2,6-diphenylpyridinium perchlorate. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
N(1)	3250(2)	3683(2)	6461(2)	45(1)
C(1)	2538(3)	4449(4)	6805(3)	64(1)
C(2)	3275(3)	3704(3)	5524(2)	45(1)
C(21)	2483(3)	4334(3)	4778(2)	52(1)
C(22)	1427(3)	4117(4)	4629(3)	65(1)
C(23)	715(4)	4704(5)	3918(4)	87(2)
C(24)	1042(5)	5494(4)	3357(3)	83(2)
C(25)	2072(4)	5699(4)	3490(3)	77(1)
C(26)	2809(4)	5113(3)	4197(2)	61(1)
C(3)	4032(2)	3099(3)	5244(2)	45(1)
C(4)	4757(2)	2442(3)	5907(2)	44(1)
C(41)	5507(2)	1714(3)	5590(2)	44(1)
C(42)	5302(3)	1396(3)	4621(2)	51(1)
C(43)	5947(3)	649(3)	4322(3)	54(1)
C(44)	6785(2)	211(3)	5007(3)	50(1)
N(2)	7426(2)	-639(3)	4682(3)	66(1)
O(1)	7352(3)	-731(3)	3823(3)	91(1)
O(2)	7968(3)	-1247(3)	5313(3)	102(1)
C(45)	7028(2)	522(3)	5968(3)	56(1)
C(46)	6388(2)	1280(2)	6252(2)	52(1)
C(5)	4687(2)	2432(2)	6856(2)	46(1)
C(6)	3938(2)	3043(3)	7134(2)	42(1)
C(61)	3844(2)	2979(3)	8140(2)	44(1)
C(62)	2984(3)	2482(3)	8337(3)	53(1)
C(63)	2930(3)	2400(3)	9288(3)	60(1)
C(64)	3729(3)	2822(3)	10034(3)	60(1)
C(65)	4578(3)	3312(4)	9842(3)	65(1)
C(66)	4636(3)	3382(4)	8890(3)	58(1)
Cl	9854(1)	1169(1)	7847(1)	65(1)
O(3)	8968(2)	1834(3)	7832(2)	77(1)
O(4)	10440(3)	969(3)	8811(2)	85(1)
O(5)	10478(3)	1749(8)	7373(4)	211(4)
O(6)	9501(4)	151(5)	7391(5)	185(3)

tuted benzene ring or contributions of canonical structures to both these rings, and are estimated by use of the HOSE-model.²³

A thorough analysis of the geometrical parameters of all substituted species considered in this paper allowed us to draw a number of conclusions. Variation of the geometry of the 4-substituted benzene ring is not regular and not very significant. In contrast, the pyridine ring undergoes significant changes in geometry. Variation of the geometry in the C3C4C41 and C5C4C41 fragments (Scheme 1) of the title compounds follows some regularity: (a) C4–C41 bond lengths (d in Scheme 1) decrease with a decrease of the C3C4C5 angle (α in Scheme 1). This is shown graphically in Fig. 1; (b) mean bond lengths (\bar{c} in Scheme 1) of C3C4 and C4C5 (c_1 and c_2 in Scheme 1) increase with a decrease of the α -angle (see Fig. 2); (c) a very rough dependence of d on the mean bond lengths c is observed (see Fig. 3).

The above relationships may be rationalized in the following way. In the case of the nitro substituent there are no push–pull interactions between the substituent and the pyridine ring. For other, more electron-donating substitu-

Table 7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1-methyl-4-(4-dimethylphenyl)-2,6-diphenylpyridinium perchlorate. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
N(1)	633(3)	2165(2)	7381(2)	44(1)
C(1)	158(6)	1596(2)	6762(2)	65(1)
C(2)	870(4)	1963(2)	8166(2)	45(1)
C(21)	765(5)	1157(2)	8372(2)	55(1)
C(22)	-581(7)	912(3)	8731(3)	78(1)
C(23)	-736(11)	172(3)	8958(4)	108(2)
C(24)	441(13)	-308(4)	8833(3)	120(3)
C(25)	1857(11)	-98(3)	8500(4)	112(2)
C(26)	2025(8)	660(3)	8243(3)	86(2)
C(3)	1189(5)	2496(2)	8740(2)	50(1)
C(4)	1281(5)	3285(2)	8560(2)	49(1)
C(41)	1671(5)	3832(2)	9168(2)	54(1)
C(42)	1481(5)	3716(2)	9961(2)	55(1)
C(43)	1841(5)	4261(2)	10527(2)	59(1)
C(44)	2433(6)	4964(2)	10335(2)	64(1)
N(2)	2809(6)	5516(2)	10893(2)	81(1)
C(441)	2640(10)	5380(3)	11725(3)	97(2)
C(442)	3299(11)	6258(3)	10657(4)	109(2)
C(45)	2635(8)	5082(3)	9544(3)	93(2)
C(46)	2254(8)	4539(3)	8988(3)	84(2)
C(5)	1002(5)	3492(2)	7746(2)	55(1)
C(6)	705(4)	2900(2)	7173(2)	47(1)
C(61)	491(5)	3114(2)	6321(2)	54(1)
C(62)	-829(6)	3551(3)	6017(2)	74(1)
C(63)	-982(8)	3787(3)	5226(3)	93(2)
C(64)	148(8)	3562(3)	4749(3)	92(2)
C(65)	1474(8)	3117(3)	5045(3)	81(1)
C(66)	1656(6)	2895(3)	5830(2)	69(1)
Cl(1)	5678(1)	2233(1)	7321(1)	93(1)
O(1)	7058(8)	2295(6)	7883(5)	214(4)
O(2)	6132(11)	2406(5)	6605(4)	206(3)
O(3)	4723(17)	2925(7)	7450(9)	157(6)
O(4)	5982(28)	1399(9)	7456(9)	206(7)
O(5)	4479(12)	1718(6)	6976(8)	139(4)
O(6)	4416(16)	2356(13)	7689(9)	205(8)

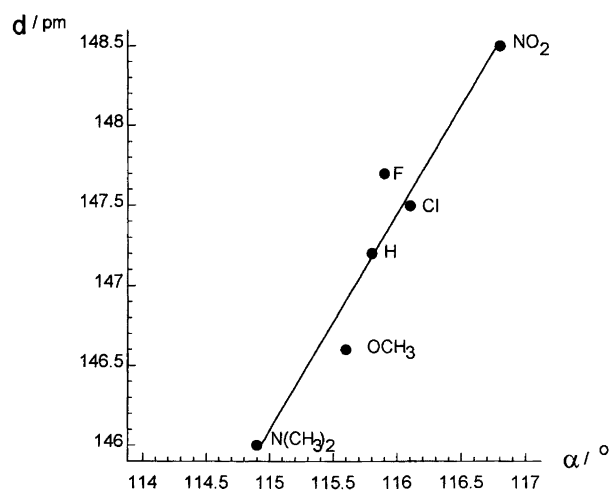


Fig. 1. Dependence of C4–C41 interatomic distance (d) on C3–C4–C5 bond angle (α); correlation coefficient $r=0.966$.

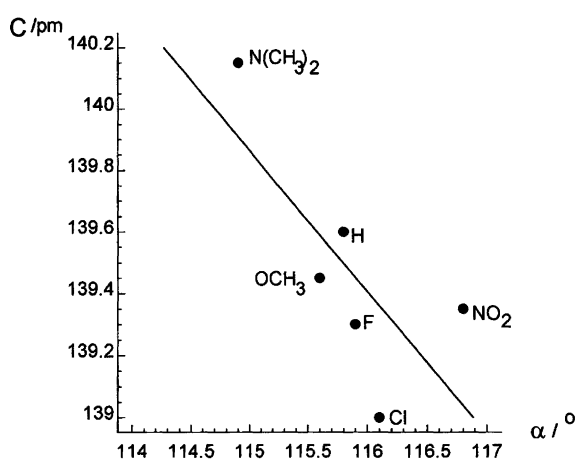


Fig. 2. Dependence of mean bond lengths $c=(c1+c2)/2$ on C3-C4-C5 bond angle (α); correlation coefficient $r=0.740$.

ents one may expect an increase in the contribution of the quinoid canonical structure as a result of a mesomeric effect of the substituent from position 4 to the pyridine ring. For these cases it is simply a tendency of the π -electron system to form localized (alternated) bonds. As a result, the d-bond becomes shorter and due to this shortening some changes in hybridization at C4 occur. In the direction of d a lower contribution of 2p in sp^2 takes place ($sp^{2-\delta}$) whereas in the direction of both C3C4 and C4C5 bonds an increased contribution of 2p is expected ($sp^{2+\delta/2}$), as shown in Fig. 4. This mechanism of rehybridization of σ -orbitals at C4 explains the observed changes in geometry: $sp^2 \rightarrow sp^{2+\delta/2}$ accounts well for the decrease of the angle between the c1 and c2 bonds and their lengthening (Schemes 1 and 2), while d is shortened. This interpretation may be understood as an extension of the Bent-Walsh rule.^{24,25} The changes in hybridization of sp^2 carbon atoms are driven by the π -electron structure which, due to the mesomeric effect (push-pull), result in localization of double and single bonds and hence affect

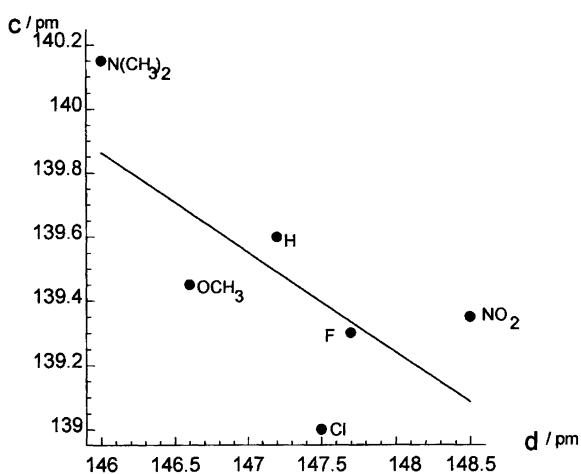


Fig. 3. Dependence of $c=(c1+c2)/2$ on d; correlation coefficient $r=0.705$.

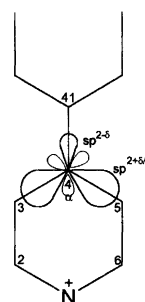


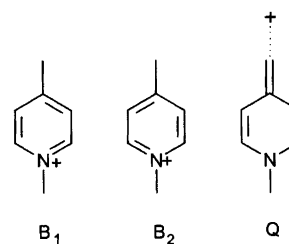
Fig. 4. Scheme of changes in hybridization at C4 as a result of C4-C41 (d) bond shortening.

the hybrid orbitals in the σ -core from sp^2 to $sp^{2+\delta}$ (the sign at δ depending on the local situation).

The above mentioned mesomeric effect, observed as a shortening of the d bond, should be accompanied by an increase in the contribution of the quinoid canonical structure Q (Scheme 3) of the pyridine ring. Application of the HOSE-model²³ enabled us to estimate weights of the canonical structures (Scheme 3) which should be understood as estimated only for the pyridine ring being the part of a classical canonical structure with exocyclic bonds, as is usual for quinoid structures. Fig. 5 presents the statistically independent quantities which are relatively well correlated, supporting the interpretation in terms of mesomeric effect between R and the pyridine ring.

It is well known^{14,16} that the localization of the π -bonds, i.e., an increase in alternation of double and single bonds in a molecule is a characteristic feature of a decrease of aromaticity. Application of the HOMA index of aromaticity,²² which is determined directly from the bond lengths of the molecular fragment, shows that a shortening of the d-value (and hence an increase of %Q, Fig. 5) is associated with a decrease in aromatic character in the pyridine ring, as shown in Fig. 6.

Owing to the bulkiness of the methyl group attached to the nitrogen ring atom there are no clear effects observed in the bond angles at C2 and C6. Mean values of the two exocyclic bond angles N1C2C21 and C3C2C26 (N1C6C61 and C5C6C66) (ϕ_1, ϕ_2 in Scheme 1) are close to 120° and no effect of electronegativity of the nitrogen atom in the $N^+ - Me$ fragment is observed. This is at variance with the dramatic changes of bond angles observed in the above positions in pyrylium salts,¹⁴⁻¹⁷ and even in



Scheme 3.

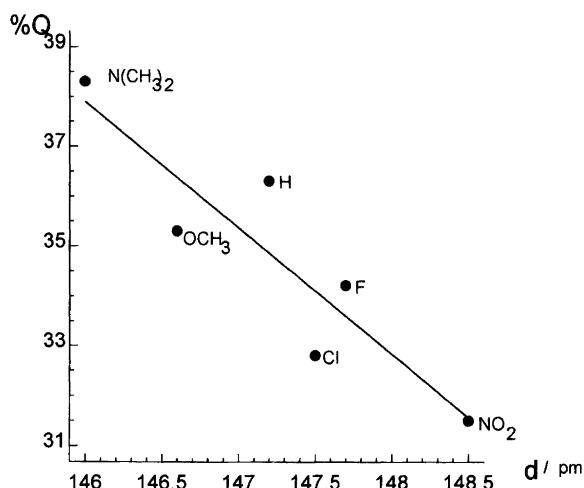


Fig. 5. Dependence of weight of quinoid structure (see Q Scheme 3) on interatomic distance C4–C41 (d); correlation coefficient $r=0.904$.

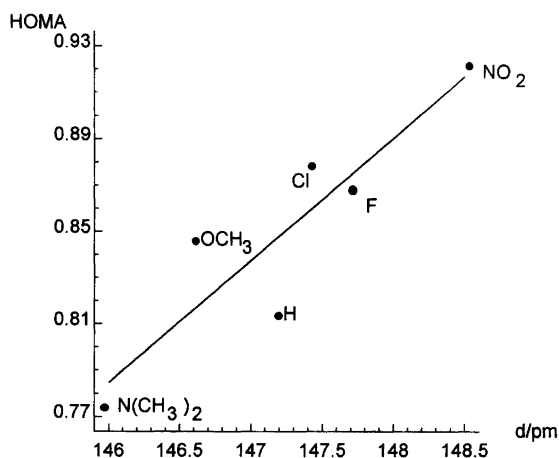


Fig. 6. Dependence of aromaticity index HOMA calculated for the pyridinium ring on the interatomic distance C4–C41 (d); correlation coefficient $r=0.904$.

4-aryl-2,6-diphenylpyridines.²⁶ Evidently, the steric effect due to the repulsion between the Me group at N1 and *ortho* atoms in both phenyl groups compensates partly the opposing effect that would stem from the electronegativity of the nitrogen atom. The above mentioned repulsion (see short contacts between the Me group and the *ortho* H-atoms in phenyl rings) is partly compensated by the torsion about C2–C21 and C6–C61, the torsion angle being about $60 \pm 10^\circ$; for details see Table 2. The situation differs from that in 2,6-pyridine derivatives where the Me group is replaced by H, i.e., for the derivatives which form complexes with acids. The release of 12 structures (flag AS1) from the Cambridge Structural Data Base²⁸ shows that if N⁺–Me is replaced by N⁺···H the enhanced electronegativity of the nitrogen atom causes typical deformations of bond angles at C2 and C6 which obey the Bent–Walsh rule. Indeed, the mean bond angles

for ϕ_1 and ϕ_2 in 2,6-substituted pyridine complexes with acids are 118.1° and 123.2° . They are smaller than those in the pyrylium salts, 113.1° and 127.4° , respectively, indicating a lower electronegativity of N⁺–H than of the oxygen atom in the pyrylium ring.

It may be concluded that the positively charged nitrogen atom in both N–H and N–Me pyridinium salts affects the hybridization at C2 and C6 but in the latter case (the title compounds) the bulkiness of the Me group at nitrogen acts against effects due to the changes in hybridization and the overall result is that there is no change in the bond angles at these carbon atoms.

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