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TRANSMISSION OF ELECTRONIC EFFECTS IN 4-ARYL-2,6-DIPHENYLPYRYLIUM PERCHLORATES AND RELATED COMPOUNDS

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Substituent effects on the ^{13}C NMR spectra of 4-aryl–2,6-diphenylpyrylium and 1-methyl-4-aryl-2,6-diphenylpyridinium perchlorates and 4-aryl-2,6-diphenylpyridines were investigated. The dual substituent parameter approach indicates that the resonance contribution to the carbon chemical shifts in the *para* position to the substituent in the 4-aryl moiety is comparable to that for 4-R-biphenyls. Although heterocyclic moieties jointed at the *para* position with respect to the substituent in the 4-aryl group differ in their deactivating power, they diminish the resonance term to the same extent in each series. This may result in conformational variations of the compounds studied. AM1 calculations were used to explain the chemical shifts observed.

INTRODUCTION

Although 1,4-disubstituted benzenes have been widely discussed based on structure–reactivity relationships,[1,2] those carrying bulky electron-accepting groups have received considerably less attention. Recently, we presented a comparative multinuclear magnetic resonance study on 2,4,6-triarylpyrylium and 1-methyl-2,4,6-triarylpyridinium perchlorates and related pyridines[3] which formally can be treated as 1,4-disubstituted benzenes.

The ^{13}C NMR spectra of some 1-substituted 2,4,6-triarylpyridinium salts[4–7] and 2,6-diarylpyrylium cations[8] have been discussed. However, no attention has been paid to the transmission of substituent effects. Because of the great importance of 4-(4-R-phenyl)-2,6-diphenylpyrylium and 1-methyl-4-(4-R-phenyl)-2,6-diphenylpyridinium salts and 4-(4-R-phenyl)-2,6-diphenylpyridines from synthetic[9] and physicochemical points of view,[10–12] it seems worth analysing the substituent effect on the basis of ^{13}C NMR spectroscopy. Consequently, 35 compounds were chosen as suitable models to investigate this problem. Simultaneously, an AM1 study was undertaken in order to explain the variations in the carbon chemical shifts.

EXPERIMENTAL

The ^{13}C NMR spectra of approximately 0·12 M solutions in DMSO-d_6 were recorded at 20 °C on a Varian Gemini 200 spectrometer in the Fourier transform mode at 50 MHz. DMSO-d_6 was used as an internal lock, and chemical shifts (δ, ppm) refer to its central peak (39·50 ppm). The spectral width was 10 000 Hz with 32K 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 broadband (BBP) and DEPT spectra[13] spectra were recorded.

All compounds studied were prepared and purified according to literature procedures.[9,10]

The AM1 semi-empirical calculations were performed according to Dewar *et al.*[14] using the AMPAC Program Package (Version 3.01) with complete geometry optimization.

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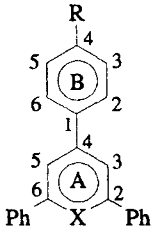
RESULTS AND DISCUSSION

The selected ^{13}C NMR chemical shifts[15] of 4-(4-R-phenyl)-2,6-diphenylpyrylium perchlorates (series **1**), 4-(4-R-phenyl)-2,6-diphenylpyridines (series **2**) and 1-methyl-4-(4-R-phenyl)-2,6-diphenylpyridinium perchlorates (series **3**) are reported in Table 1. The ^{13}C NMR spectra of some compounds studied have been measured[3,6] for a variety of solvents, high concentrations and temperatures with an insufficient set of substituents, and are therefore not appropriate for a quantitative evaluation of electronic interactions. These inadequacies were avoided in the present work.



series 1

$X = O^{+}ClO_4^{-}$

series 2

$X = N$

series 3

$X = N^{+}-MeClO_4^{-}$

In the pyrylium, pyridinium and pyridine moieties, unlike the benzene ring, the heteroatom acts as a functional centre and being an electron-withdrawing group polarizes the ring towards itself, both inductively and mesomerically.[3] Since pyrylium and pyridinium cations and also pyridine itself are isoelectronic with benzene, an interesting comparison can be made between the ^{13}C NMR chemical shifts of the series studied and those of mono- and 1,4-disubstituted benzenes.

Reasonably good correlations were obtained for the ring B carbon chemical shifts of the compounds studied and those of monosubstituted benzenes[16,17] (Table 2). The influence of 2,4,6-triphenylpyrylium and -pyridinium and pyridine moieties on the chemical shifts of C-1 is shown in Figure 1, where they are plotted against those of the corresponding monosubstituted benzenes. As seen, the cross-correlation obtained for 4-R-biphenyl derivatives[18] differs from those for series **1**–**3**.

We therefore attempted to group the chemical shift values for series **1**—**3** into two sets: the first including electron donors and hydrogen and the second including electron acceptors and hydrogen. This indicates that the ability of electron-donating substituents in the systems studied to influence the chemical shifts under consideration is more important than that for electron-withdrawing groups. For biphenyls (all substituents included) the correlation parameters are as follows: slope, $A = 1{\cdot}98$ ($\pm 0{\cdot}58$); intercept, $C = 112{\cdot}7$ ($\pm 3{\cdot}3$); correlation coefficient, $R = 0{\cdot}999$; standard deviation, $s = 0{\cdot}310$; number of points, $n = 11$. The slope reflects the larger electronic interaction of the substituent occurring in biphenyls than in the compounds investigated.

The chemical shifts of C-1 (ring B) depend linearly on the σ_p^+ parameters. The results are as follows: $A = 7{\cdot}88$ ($\pm 0{\cdot}66$), $C = 131{\cdot}1$ ($\pm 0{\cdot}4$), $r = 0{\cdot}970$, $s = 1{\cdot}489$, $n = 11$ (series **1**); $A = 10{\cdot}60$ ($\pm 1{\cdot}62$), $C = 136{\cdot}6$ ($\pm 0{\cdot}6$), $r = 0{\cdot}942$, $s = 1{\cdot}979$, $n = 13$ (series **2**); and $A = 8{\cdot}19$ ($\pm 0{\cdot}5$), $C = 132{\cdot}3$ ($\pm 0{\cdot}4$), $r = 0{\cdot}983$, $s = 1{\cdot}173$, $n = 11$ (series **3**). The fairly comparable slopes of the correlations for series **1** and **3** and those for monosubstituted benzenes ($A = 8{\cdot}47$, $n = 14$)[1,2,16] and biphenyls ($A = 9{\cdot}59$, $n = 12$)[18] suggest similar substituent effects in all the series considered.

Table 1. ^{13}C NMR chemical shifts (δ, ppm) of heteroaromatic ring A and benzene ring B (series **1**–**3**)

		Series **1**		Series **2**		Series **3**		
Compound	Carbon	A	B	A	B	A	B	N^{+}—Me
(**a**) H	1		133·33		137·63		133·21	45·19
	2(6)	169·99	129·77	156·43	127·16	156·31	128·28	
	3(5)	115·09	129·59	116·42	129·01	124·44	130·01	
	4	165·10	134·88	149·46	128·54	154·04	131·85	
(**b**) Me	1		129·37		134·69		130·31	
	2(6)	169·58	129·87	156·44	127·10	156·24	128·30	45·16
	3(5)	114·25	130·23	116·18	129·63	124·44	130·01	
	4	164·63	146·77	149·34	138·92	153·89	142·56	
	Me		21·07		20·77		20·78	
(**c**) NMe_2	1		118·13		124·02		118·53	44·03
	2(6)	165·04	133·21	155·98	127·52	155·23	129·81	
	3(5)	112·90	109·43	114·67	111·94	121·48	111·90	
	4	158·92	155·88	149·07	150·79	153·26	152·97	
	NMe_2		39·78		39·05		39·03	

(continued)

Table 1. *Continued*

Compound	Carbon	Series 1		Series 2		Series 3		
		A	B	A	B	A	B	N^+—Me
(d) NMe_2^+	1				139·47			
	2(6)			157·02	129·56			
	3(5)	No compound		116·95	121·41	No compound		
	4			148·04	147·72			
	NMe_3^+		56·51					
(e) OMe	1		124·11		129·73		125·15	44·98
	2(6)	168·67	132·68	156·33	128·46	156·03	130·38	
	3(5)	113·02	115·29	115·77	114·36	123·72	114·93	
	4	163·48	165·70	148·94	160·25	153·43	162·73	
	OMe	55·88		55·20		55·54		
(f) SMe	1		127·71		133·86		129·06	44·64
	2(6)	169·11	130·12	156·51	127·65	156·33	128·87	
	3(5)	113·58	125·58	116·04	126·03	124·22	125·80	
	4	163·57	150·18	148·80	140·06	153·33	144·80	
	SMe	13·76		14·42		13·97		
(g) CF3	1		136·34		141·71		137·28	45·38
	2(6)	170·66	130·34	156·62	128·17	156·57	129·22	
	3(5)	116·28	127·63	116·72	125·65	125·73	125·84	
	4	163·71	133·42	147·95	129·78	152·46	131·41	
	CF_3	123·37		124·08		123·54		
(h) F	1		128·33		134·01		129·71	45·45
	2(6)	169·89	132·93	156·41	129·13	156·29	131·06	
	3(5)	114·83	116·76	116·25	115·67	124·83	116·28	
	4	163·74	166·19	148·28	167·78	152·85	164·38	
(i) Cl	1		129·90		136·37		132·12	45·46
	2(6)	170·00	131·80	156·50	128·83	156·46	130·28	
	3(5)	115·10	131·50	116·25	129·05	125·06	129·37	
	4	163·70	131·50	148·06	134·05	152·72	137·17	
(j) Br	1		131·17		136·78		132·50	45·48
	2(6)	170·09	131·45	156·55	129·14	156·49	130·41	
	3(5)	115·01	132·55	116·26	131·83	125·02	132·34	
	4	163·82	128·34	148·18	123·79	152·84	126·14	
(k) CO_2Me	1		135·66		142·15		137·45	45·44
	2(6)	170·39	129·59	156·65	127·44	156·53	128·72	
	3(5)	115·78	128·39	116·71	129·74	125·56	129·67	
	4	165·99	135·92	148·23	130·04	152·70	132·18	
	CO	164·05		165·91		165·31		
	Me	52·08		52·29		52·16		
(l) $CONH_2$	1				141·63			
	2(6)			156·55	127·33			
	3(5)	No compound		116·51	129·71	No compound		
	4			148·33	131·23			
	CO			166·75				
(m) NO_2	1		138·13		143·96		139·28	45·52
	2(6)	170·80	131·00	156·67	128·57	156·64	129·85	
	3(5)	116·46	123·98	116·74	123·79	125·98	123·85	
	4	163·20	150·44	147·14	147·74	151·71	149·14	

Table 2. Correlations[a] between the ^{13}C NMR chemical shifts of the benzene ring B for series **1**–**3** and those for monosubstituted benzenes[16]

			Chemical shift (δ, ppm), R = H				
Series	Carbon	*A* (±*a*)	Exptl.	Calcd	*n*	*r*	*s*
1	C-1[b]	1.26 (±0·07)	133·33	133·28	8	0·991	0·707
	C-2(6)	1·49 (±0·47)	129·77	123·72	11	0·923	0·976
	C-3(5)	1·08 (±0·08)	129·59	127·38	11	0·974	1·796
	C-4	0·95 (±0·07)	134·88	134·79	11	0·978	2·852
2	C-1[b]	1·17 (±0·06)	137·63	137·75	8	0·993	0·559
	C-1[c]	1·04 (±0·12)	137·63	137·52	6	0·975	0·554
	C-2(6)	0·93 (±0·12)	127·16	127·39	13	0·921	0·339
	C-3(5)	1·04 (±0·03)	129·01	128·81	13	0·996	0·718
	C-4	1·07 (±0·03)	128·45	127·80	13	0·995	1·467
3	C-1[b]	1·26 (±0·08)	133·21	133·29	8	0·987	0·839
	C-2(6)	1·35 (±0·01)	128·28	128·57	11	0·938	0·343
	C-3(5)	1·11 (±0·03)	129·19	128·81	11	0·996	0·707
	C-4	0·97 (±0·04)	131·85	131·55	11	0·992	1·754

[a] *A*, slope; *a*, error of the slope; *n*, number of points; *r*, correlation coefficient; *s*, standard deviation.
[b] Electron-donating substituents and hydrogen were included.
[c] Electron-withdrawing groups and hydrogen were included.

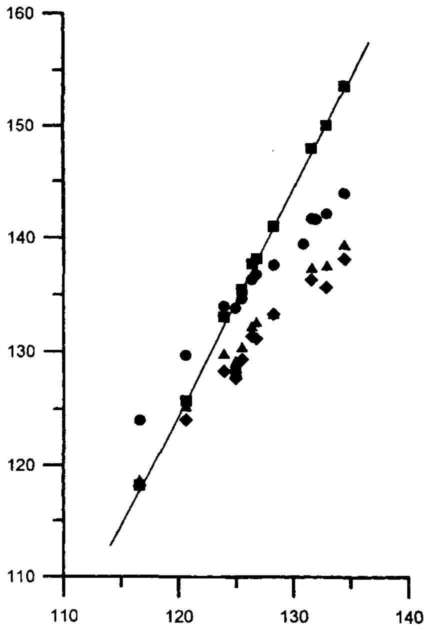


Figure 1. Relationship of the carbon chemical shifts (δ, ppm) of C-1 (ring B) for series **1**—**3** and 4-R-biphenyls *vs* those for monosubstituted benzenes where ◆, ●, ▲ and ■ refer to points for series **1**, **2**, **3** and 4-R-biphenyls, respectively

The dual substituent parameter (DSP)[20,21] treatment allows the estimation of both inductive and resonance contributions to the chemical shifts of C-1 (ring B) for series **1**–**3** and 4-R-biphenyls. Correlations were carried out using various scales,[19–21] and no significant differences were noted in the values of regression parameters, i.e. ρ_I and ρ_R as well as the goodness of fit.[20c,21] The set of σ_I and σ_R constants were used and data are collected in Table 3. This model explains more than 97% of the observed variations in the chemical shifts. The results in Table 3 show that the substituent chemical shifts are more sensitive to the resonance effect than to an inductive influence, and resonance contributions are almost most twice as large as inductive contributions. However, the increase in both ρ_I and ρ_R values in the case of 4-R-biphenyls indicates that the carbon chemical shifts are more sensitive to the substituent electronic effect than those in the series **1**–**3**. In both mono- and 1,4-disubstituted benzenes carrying electron-withdrawing groups,[2] the ratio of susceptibility parameters, $\lambda = \rho_R/\rho_I$, reflects a strong increase in the relevance of resonance interactions. Thus, for monosubstituted benzenes (PhR) $\lambda = 4{\cdot}7$, and for 1,4-disubstituted benzenes it varies between 3·5 and 8·0, being exceptionally high for nitro derivatives (17·1).[2] The mean value of λ, calculated from the data in Ref. 2, is 5·4 (NO_2 excluded) or 6·1 (NO_2 included). Hence one would suggest that in the series under study the electronic effect of the variable group is suppressed by the heterocyclic moiety and the 4-R substituent is not a strongly cross-interacting one.

Table 3. DSP correlations[a] of the ^{13}C NMR chemical shifts of C-1 (ring B) in series **1**–**3** and in 4-R-biphenyls (4-BPh)[18]

Series	ρ_I ($\pm a$)	ρ_R ($\pm \beta$)	C ($\pm c$)	λ	r	s	F	n
1	7·94 (±1·27)	15·52 (±0·78)	132·11 (±0·20)	1·95	0·991	0·860	223	11
2	6·95 (±1·06)	15·57 (±0·82)	138·01 (±0·19)	2·24	0·988	0·937	205	13
3	9·17 (±0·91)	15·73 (±0·56)	132·75 (±0·14)	1·72	0·996	0·618	457	11
4-BPh	15·05 (±2·89)	27·47 (±1·78)	140·55 (±0·45)	1·85	0·986	1·050	138	11

[a] $\sigma_I$and σ_R were used as the substituent constants and were taken from Ref. 19. ρ_I and ρ_R are the correlation parameters, C is the intercept; a, b and c

As seen, the variations of the chemical shifts in series **1**–**3** are much less important than those observed in the case of 4-R-substituted biphenyls. This is undoubtedly due to the electron-withdrawing character of the heteroaryl moiety in the *para* position to the variable 4-R group. Competitive interactions between electron-donating substituent and acceptors, such as both charged oxygen and nitrogen and the aza atom, result in a decrease in the overall substituent chemical shifts (SCSs). The true dependence between the electronic character and the chemical shift observed seems to be a complex relationship involving the type of heteroatom and conformational variations [see x-ray results[11,12] and AM1 calculations (this work)].

The ability of different substituents to delocalize the positive charge from the electron-deficient centre has been discussed by Farcasiu and Sharma.[8] Moreover, it is well documented that the electron-donating property of the group is determined by the electron demand from the deficient centre.[2] In the case of 1,4-disubstituted benzenes, the π-electron donation increases and π-electron withdrawal decreases when the group in the *para* position becomes increasingly π-electron withdrawing.[2,16] The positive charge in positions 2(6) and 4 (ring A) in the series studied should increase in the same manner the electron-donating property of the substituent. Here, however, this may be attributed to the nature of the heteroatom: the effect of charge delocalization in the pyrylium cation is more evident than in the pyridinium cation. Moreover, it seems that anisotropic effects of the benzene rings in positions 2(6) contribute to the chemical shifts in a way independent of the electronic properties of the substituent.[5]

In general, quaternization of the pyridine ring nitrogen atom deshields signals of C-3(5) and C-4 more strongly than 2(6) signals.[16] The relative chemical shift differences (CSD) Cor series **2** and **3** can be obtained from the data in Table 1. Thus, the CSDs for C-4 (ring A) are almost constant (4·6 ppm) except for R = NMe_2 (4·1 ppm). The corresponding effect is 11·1 ppm for pyridine itself and 1-methylpyridinium cation.[6,16] The largest CSD is observed for C-3(5) varying from 6·8 ppm (R = NMe_2) to 9·3 ppm (R = NO_2). In case of C-2(6) the effect is almost vanishing. Calculations of the C—N bond order changes indicate the increase in the charge density variations and decrease in the total π-bond order change on going from pyridine to phenylpyridine. This reinforces the decrease in the low-frequency shift of C-2(6) and indicates that 4-R-phenyl groups modify the sensitivity of the *ipso* carbon chemical shift to the substituent effect similarly in a charged system such as series **3**.

A comparison of the ^{13}C NMR chemical shifts for the parent compounds, **1a**–**3a** (Table 1), with those of unsubstituted pyrylium and *N*-methylpyridinium cations and pyridine,[16] respectively, indicates that in the case studied the signals of C-4 and C-2(6) are in a downfield position except those for C-2(6) in **3a**; nonetheless, it is well established that the electron deficiency is the highest for unsubstituted compounds.[2,8,18] The corresponding downfield shifts for C-4 are 4, 14 and 20 ppm for **1a**, **2a** and **3a**, respectively. This seems to reflect variations in the twist angle of the benzene rings in positions 4 and 2(6).

Experimental chemical shifts are frequently related to the calculated changes in electron density.[23] In our study, the calculations allow a better insight into the extent of the substituent effect in the case of the parent compounds **1a** and **2a** as well as 1-methyl-4-aryl-2,6-diphenylpyridinium cations (series **3**). For this purpose the AM1 formalism[14] was employed in the present work. Bond lengths and valence angles were fully optimized. Table 4 gives selected results of those calculations.

Palmer *et al.*[24] found that the valence electron distribution in the pyrylium cation indicates a slight negative charge at the oxygen and a higher positive charge at C-2(6) than C-4. The major part of the positive charge is localized on hydrogen atoms. Calculations performed here support this and show that the coplanar structure of **1a** is about 1·5–2·0 kcal mol^{-1} higher in energy than the twisted structure. Thus, the resonance structures based on the polarization of the π-electrons alone provide an inadequate picture of the pyrylium moiety. It should be mentioned that Fromberz and Heilemann[25] found from MNDO calculations that both rings in 1-methyl-4-(4′-dimethylaminophenyl)pyridinium tetrafluoroborate are twisted by 49° and 84% of the positive charge is in the pyridinium moiety. Inspection of the carbon chemical shifts

Table 4. The AM1 calculation results for 2,4,6-triphenylpyrylium perchlorate (**1a**), 2,4,6-triphenylpyridine (**2a**) and 1-methyl-4-aryl-2,6-diphenylpyridinium perchlorates, series **3**

	Net charge (a.u.)								
	Ring A			Ring B					
No.	C-3	C-4	$O^+/N/N^{+a}$	N^+-Me[b]	C-1	C-4	α^c	β^d	d[e]
1a	0·2374	−0·1808	0·0735	—	0·1314	0·0630	34·1	19·2	1·447
2a	0·1654	−0·0038	0·1237	—	0·0503	0·1208	40·7	43·9	1·451
3a	0·1596	−0·1179	0·0437	0·1262	0·1178	0·0758	34·8	61·4	1·452
3b	0·1620	−0·1271	0·0451	0·1258	0·1289	0·0046	33·2	61·6	1·450
3c	0·1822	−0·1527	0·0607	0·1242	0·2039	−0·1934	24·1	62·1	1·434
3e	0·1683	−0·1330	0·0497	0·1247	0·1672	−0·1557	30·7	62·2	1·445
3f	0·1637	−0·1242	0·0464	0·1257	0·1366	0·1535	32·1	61·6	1·448
3g	0·1535	−0·1019	0·0374	0·1282	0·0847	0·1186	37·5	61·3	1·455
3h	0·1613	−0·1189	0·0392	0·1307	0·1364	−0·1555	34·0	61·3	1·450
3i	0·1589	−0·1149	0·0376	0·1311	0·1183	0·0093	34·7	61·2	1·452
3k	0·1543	−0·1055	0·0345	0·1322	0·0870	0·0611	36·9	61·2	1·455
3m	0·1662	−0·1110	0·0772	0·1325	0·0723	0·0934	38·9	59·2	1·457

[a] Means net charge for O^+, N and N^+ atoms for pyrylium cation, pyridine and pyridinium cations, respectively.
[b] The same for the carbon of the N^+ -Me group.
[c] Twist angle between rings A and B.
[d] Twist angle between rings A and C.
[e] C-4 (ring A)—C-1 (ring B) distance.

indicates that there is more positive charge in the heteroaryl moiety of **1a**–**3a** than in the benzene ring in position 4.

Calculated net charges (Table 4) explain the variations in the chemical shift values. Thus, for position 4 (ring A) the positive charge changes in order **1a** > **3a** > **2a** that follows the chemical shift variations.[3] Moreover, since AM1 calculations show in fact a slight excess charge density at position 4 (ring B) and a high positive charge at position 4 (ring A) for series **3**, this means that the transmission of the substituent effect in the charged system cannot be overestimated in the solution.

In case of the parent compounds **1a**–**3a**, a downfield shift for C-4 (rings A and B) and an upfield shift for C-1 (ring B) is observed as compared with that for 4-R-biphenyls.[18] Thus, the largest downfield effect means the strongest localization of the positive charge in case of the pyrylium cation, **1a**, according to the AM1 calculations. For 2,4,6-triphenylpyridine C-4 resonates at 129·2 ppm, this value being the nearest to biphenyl (128 ppm).[16] However, the magnitudes of net charge for the parent molecules for heteroatom: $N^+ < O^+ < N$ may result in an orientation of the 4-R-substituted and 2(6) benzene rings against the heteroaryl moiety. The two angles are not equal, and are different for the particular series studied. Small torsional angles between the benzene rings in positions 2(6) and the pyrylium ring were confirmed to appear in the molecule on the basis of x-ray measurements in case of series **1**.[11] Hence one would suggest that the chemical shifts studied reflect the complex effects involving both the heteroatom influence and conformational variations.

The experimental chemical shifts of C-1 for series **3** (ring B) have been related to the calculated net charges. Thus, there is a linear relation of the ^{13}C NMR data for carbons in that position, covering a range of 28 ppm and a total representation of substituents required for the description of the substituent effect by means of the similarity model[20] *vs* net charge values (Δq_c) for those carbon atoms. The correlation results are $r = 0{\cdot}998$, $s = 0{\cdot}440$, $n = 10$. The slope is equal to 156·65 (±3·71) ppm per electron. The correlation results for the carbon chemical shifts of C-3(5) (ring A) are worse and only 75% of the observed variations in chemical shifts may be verified by use of the net charge data When the most deviating point, *i.e.* R = NO_2, is excluded the results are $A = 147{\cdot}29$ (±5·11), $r = 0{\cdot}996$, $s = 0{\cdot}125$, $n = 9$. Hence the chemical shifts considered appear to be a quantitative indicator of the charge distribution in the system studied.

A comparison of C-4 chemical shifts (ring A, series **3**) and charge densities clearly shows that the extent of conjugative interaction is a function of the relative orientation of the benzene ring considered and the electron-deficient centre.[8] This must be taken into account for the evaluation of the electronic effect of phenyl and 4-aryl groups. The deviation from the coplanarity decreases the conjugation in biphenyls[18] and influences the solvolysis rates of some 4-substituted aryl halides.[26] In this study, the differentiation of the electron-donating ability is clear for pyrylium cations ($\Delta\delta = 6{\cdot}18$ ppm) and much less clear for series **2** (2·32 ppm) and series **3** (2·33 ppm) and also biphenyls (2·40 ppm).[1]

It seems that the electron-donating or -accepting ability of the 4-aryl group quantified in terms of their ^{13}C chemical shifts is due to changes in the total electron density induced in the heterocyclic ring as a site probe.

The calculated twist angles, α, and bond distances, d, (see Table 4) between 4-aryl and pyridinium moieties (series **3**) follow the electronic character of substituent. Thus, smaller angles were found for electron donors and larger angles for electron acceptors. On the other hand, both the C-4 (ring A)—C-1 (ring B) bond distance and twist angle increase, resulting in a downfield shift on going from NMe_2 to NO_2. The magnitude of the twist angle indicates the decrease in the electronic competitions in the case of electron-withdrawing groups.

Conformational preferences of both the aromatic and heteroaryl rings in the series studied could be explained by the available experimental gas-phase data for biphenyl derivatives without *ortho* substituents.[27] Thus, gas-phase electron diffraction results show that the sensitivity of the twist angle to the substituent effect is small.[27] The average torsion angle about the central C—C bond is 44° whereas in the solid state it is close to 0°. Small variations of the calculated twist angle for the compounds studied seem to be in a fairly good agreement with the results given above. Moreover, it was stated that in series **1** both 2(5)-phenyl and 4-aryl groups interact sterically with 3(5)-hydrogens (ring A).[11] Based on the x-ray data such an interaction is less important for series **2** and **3** because of the deviation of their molecules from planarity.[12]

Owing to the electron-donating character of the phenyl group itself, there is an effective interaction between the 4-aryl and 1-methylpyridinium moieties (series **3**). Hence the observed relative displacement of the ^{13}C SCSs of the 1-methyl function can be attributed to the long-range transmission of the electronic effect. The trend is quite quantitative as seen by the fit of the correlation between the chemical shifts and σ_{p+} parameters ($r = 0{\cdot}927$).[19] Thus, NMe_2 produces the maximum upfield and NO_2 the maximum downfield shift as compared with the unsubstituted parent compound **3a**. The difference in electron density is as large as 0·00735 electrons and corresponds to a difference of 1·5 ppm following the model [for C-1 (ring B) 0·0095 electrons]. Unfortunately, the charges calculated for the nitrogen atom of the N^+-Me group do not reflect the variations in the chemical shifts of the methyl function. This may be due to the steric effect of the methyl group.[12]

Generally, the AM1 calculations indicate that the geometry of the 1-methyl-2,4,6-triphenylpyridinium cation is not appreciably modified by *para* substituents (ring B), even for strong electron-withdrawing or donating groups. This is attributed to weak conjugation between the substituent and heteroaromatic ring, at least in the ground state. The substituent resonance effects are mainly localized within the 4-substituted benzene ring, although a shortened C-4 (ring A)—C-1 (ring B) bond length could suggest a strong resonance interaction between the two rings. However, the correlations of the SCSs of the compounds studied *vs* those of monosubstituted benzenes can provide useful information on the through-resonance interaction. The analysis in terms of the DSP approach shows that resonance contributions in the series studied are much less significant owing to the twist of two ring planes as stated for mono- and 1,4-disubstituted benzenes.

In conclusion, the chemical shifts in the series studied reflect the substituent influence modified by geometry changes rather than the variations in charge distribution. It seems that the results of this work provide a new insight into the quantitative nature of electronic interactions of 1,4-disubstituted benzenes having bulky conformationally flexible electron-withdrawing groups.

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REFERENCES

1. C. G. Swain and E. Lupton, *J. Am. Chem. Soc.* **90**, 432 (1968).
2. J. Bromilow, R. T. C. Brownlee, D. J. Craik, M. Sadek and R. W. Taft, *J. Org. Chem.* **45**, 2429 (1980).
3. E. Kolehmainen, D. Rasala, T. Bąk, K. Laihia, and R. Gawinecki, *Spectrosc. Lett.* **28**, 621 (1995).
4. S. R. Salman and A. H. Hassan, *Spectrosc. Lett.* **24**, 873 (1991).
5. R. M. Claramunt and J. Elguero, *Collect Czech. Chem. Commun.* **46**, 584 (1981).
6. A. T. Balaban and V. Wray, *Org. Magn. Reson.* **9**, 16 (1977).
7. A. R. Katritzky and Z. Dega-Szafran, *Magn. Reson. Chem.* **27**, 1090 (1989).
8. D. Farçasiu and S. Sharma, *J. Org. Chem.* **56**, 126 (1991).
9. T. Bąk, D. Rasala and R. Gawinecki, *Org. Prep. Proced Int.* **26**, 101 (1994), and references cited therein.
10. R. Gawinecki, T. Bąk, D. Rasala and S. Styrcz, *Pol. J. Chem.* **70**, 188 (1996).
11. (a) I. Turowska-Tyrk, R. Anulewicz, T. M. Krygowski, B. Pniewska and P. Milart, *Pol. J. Chem.* **66**, 1831 (1992); (b) I. Turowska-Tyrk, T. M. Krygowski and P. Milart, *J. Mol. Struct.* **273**, 235 (1991); (c) I. Turowska-Tyrk, T. M. Krygowski, P. Milart, G. Butt and R. D. Topsom, *J. Mol. Struct.* **245**, 289 (1991); (d) T. M Krygowski, R. Anulewicz, B. Pniewska and P. Milart, *J. Phys. Org. Chem.* **4**, 121 (1991).
12. (a) T. M. Krygowski, R. Anulewicz, A. Jarmuła, T. Bąk, D. Rasała and S. Howard, *Tetrahedron* **50**, 13155 (1994); (b) R. Anulewicz, T. Bąk, M. Cyrański, T. M. Krygowski, D. Pawlak, B. Pniewska, D. Rasała and R. Gawinecki, *Acta Chem. Scand.* **49**, 515 (1995); (c) R. Anulewicz, T. Bąk, M. Cyrański, T. M. Krygowski, D. Rasała and B. Swirska, *Pol. J. Chem.* **69**, 597 (1995).

13. J. K. M. Sanders and B. K. Hunter, *Modern NMR Spectroscopy*. Oxford University Press, Oxford (1987).
14. M. J. S. Dewar, E. G. Zoebish, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985).
15. The ^{13}C NMR chemical shifts of phenyl ring in the position 2(6) are not discussed and reported here: they are available from the authors on request.
16. (a) H.-O. Kalinowski, S. Berger and S. Brown, *Carbon-13 NNR Spectroscopy*. Wiley, New York (1988); (b) E Breitmaier and W. Voelter, *Carbon-13 NMR Spectroscopy, High Resolution Methods and Applications in Organic Chemistry and Biochemistry*. VCH, Weinheim (1987).
17. B. M. Lynch, *Can. J. Chem.* **55**, 541 (1977).
18. E. M. Schulman, K. A. Christensen, D. M. Grant and C. Walling, *J. Org. Chem.* **39**, 2686 (1974).
19. C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.* **9**, 165 (1991), and references cited therein.
20. (a) S. Ehrenson, R. T. C. Brownlee and R. W. Taft, *Prog. Phys. Org. Chem.* **10**, 3 (1973); (b) D. J. Craik and R. T. C. Brownlee, *Prog. Phys. Org. Chem.* **14**, 1 (1983); (c) T. M. Krygowski and R. I. Zalewski, *Match* **24**, 119 (1989).
21. R. I. Zalewski, T. M. Krygowski and J. Shorter, *Similarity Models in Organic Chemistry, Biochemistry and Related Fields*. Elsevier, Amsterdam (1991).
22. H. C. Brown, M. Periasamy, D. P. Kelly and J. Giansiracusa, *J. Org. Chem.* **47**, 2089 (1982).
23. S. Fliszar, G. Cardinal and M.-T. Beraldin, *J. Am. Chem. Soc.* **104**, 5287 (1982).
24. M. H. Palmer, R. H. Findlay, W. Moyes and A. J. Gaskell, *J. Chem. Soc., Perkin Trans. 2* 841 (1975).
25. P. Fromberz and A. Heilemann, *J. Phys. Chem.* **96**, 6864 (1992).
26. (a) E. Berliner and N. Schich, *J. Am. Chem. Soc.* **79**, 3849 (1957); (b) H. C. Brown, Y. Okamoto and T. Inukai, *J. Am. Chem. Soc.* **80**, 4964 (1958).
27. C. P. Brock and R. P. Minton, *J. Am. Chem. Soc.* **111**, 4586 (1989).