

INTERPRETATION OF ^1H NMR SPECTRA OF 2-BENZOPYRYLIUM SALTS WITH THE USE OF THE CNDO/2 METHOD

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The ^1H NMR spectra of eleven substituted 2-benzopyrylium salts are interpreted with the aid of the CNDO/2 method for standard geometry. Some effects of the substituents are considered for the charge distribution in the 2-benzopyrylium cation.

INTRODUCTION

The various conversions of 2-benzopyrylium salts into carbo¹⁻³ and heteroderivatives,^{4,5} which have been used for practical purposes also,^{6,7} and into different types of dimers^{8,9} and C-adducts¹⁰ require an explanation of the results on the basis of the structures of the compounds used. Fairly complete structural data for monocyclic pyrylium salts have been reported,¹¹ but so far few papers have been devoted to the 2-benzopyrylium salts with respect to the use of quantum chemical calculations for rationalization of the ^{13}C NMR spectra.^{10,12,13}

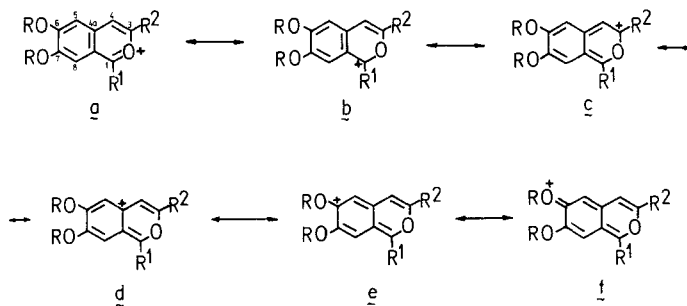
The main aim of this work was to correlate chemical shifts in the ^1H NMR spectra with the charge distribution in the cation for eleven substituted 2-benzopyrylium salts and to establish the relationship between the influence of the substituents and the charge distribution in the cation. The latter aspect determines the reactivity of the 2-benzopyrylium cation.

It should be emphasized that almost all known conversions of 2-benzopyrylium salts are the result of their reactions with nucleophiles,¹⁻¹⁰ and 2-benzopyrylium behaves chemically like a carbenium and not an oxonium salt, similarly to its monocyclic analogue.¹¹ This can be easily understood if one takes into account resonance formulae **a-f** where oxonium form **f** is excluded owing to the absence of an alkoxy substituent in position 6.

RESULTS AND DISCUSSION

The charge distribution in the 2-benzopyrylium cation was estimated by the CNDO/2 method with standard geometry, which revealed a good correlation with the ^{13}C NMR data for 2-benzopyrylium salts¹³ and cyanoisochromenes.^{10,14}

It is known that the picture of the charge distribution depends on the parameterization of the method used.¹⁵

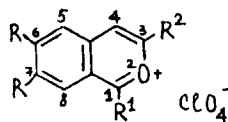


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Thus, the oxygen atom has a slightly negative charge for the 2,4,6-trimethylpyrylium cation according to the CNDO/2¹⁶ and *ab initio* STO-3G¹⁷ methods, whereas

the first calculation for 1,3-dimethyl-2-benzopyrylium **4** by the simple LCAO-MO method¹⁸ revealed a positive charge density on the oxygen atom, and its value was

Table 1. Charge densities (ΣQ) of atoms C-1 to C-8 calculated by the CNDO/2 method (standard geometry) and measured ¹H chemical shifts (δ , ppm) of substituents/hydrogen atoms for 2-benzopyrylium salts 1-15



Compound	Substituent			C-1			C-3	
	R	R ¹	R ²	ΣQ_{O-2}	ΣQ_{C-1}	δ_{R^1}	ΣQ_{C-3}	δ_{R^2}
1 ^a	CH ₃ O	H	H	-0.131	0.251	—	0.232	—
2 ²⁹	CH ₃ O	H	CH ₃	-0.168	0.240	9.17	0.313	2.42
3 ⁶	CH ₃ O	CH ₃	H	-0.151	0.291	2.93	0.224	d, 1H, 8.28 J = 6 Hz
4 ^a	H	CH ₃	CH ₃	-0.189	0.323	—	0.306	—
5 ³⁰	CH ₃ O	CH ₃	CH ₃	-0.172	0.290	2.84	0.280	2.40
6 ³⁰	CH ₃ O	CH ₂ CH ₃	CH ₃	-0.175	0.282	t, 1.18, CH ₂ CH ₃ ; q, 3.38, CH ₂ CH ₃ d, 6H, 1.63, CH(CH ₃) ₂ , J = 7 Hz; septet, 3.83, CH(CH ₃) ₂ 2.83	0.278	2.40
7 ¹⁰	CH ₃ O	CH(CH ₃) ₂	CH ₃	-0.175	0.278	d, 6H, 1.63, CH(CH ₃) ₂ , J = 7 Hz; septet, 3.83, CH(CH ₃) ₂ 2.83	0.277	2.43
8 ^b	CH ₃ O	CH ₃	CH(CH ₃) ₂	-0.175	0.280	—	0.274	d, 6H, 1.51 CH(CH ₃) ₂ , J = 7 Hz; septet, 2.83, CH(CH ₃) ₂ 2.39
9 ¹	CH ₃ O	CH ₂ C ₆ H ₅	CH ₃	-0.176	0.286	s, 4.50, CH ₂ C ₆ H ₅ ; s, 6.95, CH ₂ C ₆ H ₅ m, 7.36, C ₆ H ₅ + 1H	0.277	2.50
10 ³¹	CH ₃ O	C ₆ H ₅	CH ₃	-0.177	0.255	—	0.274	2.50
11 ^a	CH ₃ O	CH ₃	CH ₂ C ₆ H ₅	-0.177	0.280	—	0.284	—
12 ^b	CH ₃ O	CH ₃	CH ₂ C ₆ H ₅ -3,4 -(OCH ₃) ₂	-0.176	0.280	2.85	0.285	s, 3.98, CH ₂ ; s, 6H, 3.50, (CH ₃ O) ₂ ; s, 6.60, aromatic 3H —
13 ^a	H	CH ₃	C ₆ H ₅	-0.180	0.318	—	0.263	—
14 ³²	H	CH ₃	3-CH ₃ OC ₆ H ₄	-0.183	0.316	3.10	0.227	s, 3.50, CH ₃ O and m, 4H from aromatic 9H, 6.65-8.63
15 ³³	CH ₃ O	CH ₃	C ₆ H ₅	-0.176	0.278	2.93	0.259	m, 3H, 7.18 m, 2H, 7.55

^a These salts have not been synthesized.

^b For syntheses, see Experimental.

greater than the charge densities on C-1 and C-3. This assumed the main resonance contribution from oxonium form **a**.

Among semi-empirical calculations, the CNDO/2 method gives the most reliable results for the estimation of the charge distribution in the molecule and for correlations of calculated charge densities with experimental NMR data.¹⁹ The application of the CNDO/2 method to the substituted 2-benzopyrylium cations **1-15** unambiguously predicts a negative charge density on the oxygen heteroatom (Table 1), and this

value hardly depends on the substituents. These results highlight the main contribution from carbenium resonant structures **b-e** in comparison with the oxonium form **a**.

At the same time, the character of the substituents and their presence in positions 1 and 3, and the absence or presence of methoxy groups in positions 6 and 7, influence the picture of the charge distribution. This is displayed both for the calculations and for their comparison with ¹H NMR data for salts **2, 3, 5-10, 12, 14** and **15**.

$\Sigma Q_{C-1} - \Sigma Q_{C-3}$	C-4		C-5		C-8		C-6		C-7	
	ΣQ_{C-4}	δ_{H-4}	ΣQ_{C-5}	δ_{H-5}	ΣQ_{C-8}	δ_{H-8}	ΣQ_{C-6}	δ_{H-6}	ΣQ_{C-7}	δ_{H-7}
0.019	-0.088	—	-0.120	—	-0.031	—	0.256	—	0.153	—
-0.073	-0.135	7.02	-0.126	7.22	-0.037	7.67	0.248	3.85	0.151	3.71
0.067	-0.092	d, 7.63 J = 6 Hz	-0.117	7.18	-0.034	7.38	0.247	3.88	0.148	3.80
0.017	-0.135	—	-0.050	—	0.050	—	0.095	—	-0.011	—
0.010	-0.125	6.96	-0.122	7.22	-0.036	7.30	0.244	3.82	0.146	3.74
0.004	-0.128	6.98	-0.122	7.24	-0.035	7.30	0.243	3.80	0.144	3.73
0.001	-0.127	7.00	-0.122	7.30	-0.035	7.30	0.242	3.83	0.143	3.78
0.006	-0.131	7.00	-0.124	7.20	-0.039	7.30	0.242	3.83	0.146	3.77
0.009	-0.128	7.02	-0.123	7.35	-0.033	7.35	0.242	3.85	0.142	3.70
-0.019	-0.124	7.23	-0.123	7.36	-0.178	7.50	0.240	3.90	0.151	3.65
-0.006	-0.136	—	-0.124	—	-0.039	—	0.242	—	0.145	—
-0.005	-0.136	6.98	-0.124	7.21	-0.039	7.21	0.241	3.80	0.145	3.75
0.055	-0.120	—	-0.048	—	0.047	—	0.091	—	-0.010	—
0.089	-0.126	m, 1H from arom. 9H, 6.65- 8.63	-0.049	m, 1H from arom. 9H, 6.65- 8.63	0.005	m, 1H from arom. 9H, 6.65- 8.63	0.099	m, 1H from arom. 9H, 6.65- 8.63	-0.011	m, 1H from arom. 9H, 6.65- 8.63
0.019	-0.125	7.08	-0.122	7.18	-0.039	7.83	0.239	3.83	0.145	3.75

It can be seen in Table 1 that the chemical shifts of the methoxy substituents in both positions hardly depend on R¹ and R² and also the total charge densities for C-6 (ΣQ_{C-6}) and C-7 (ΣQ_{C-7}) remain unchanged. The 6-CH₃O and 7-CH₃O signals are recorded at δ 3.80–3.90 and 3.65–3.80, respectively, in accordance with the calculated data.

It should be noted that according to the calculations the methoxy groups do not have much influence on the ratio of ΣQ_{C-1} and ΣQ_{C-3} . The presence of these substituents leads only to a slight increase in ΣQ_{C-1} [compare ($\Sigma Q_{C-1} - \Sigma Q_{C-3}$) for **4** and **5** and for **13** and **15**]. The insignificant donor effect of the methoxy groups for the heterocyclic fragment of the cation is corroborated by the nearly unchanged ΣQ_{C-4} values for **4–5** and **13–15**.

However, the effect of the methoxy groups in the benzenoid ring annelated with the heterocyclic ring is strong and leads to a sharp decrease in ΣQ_{C-5} and ΣQ_{C-8} in the absence of the substituents on the 6- and 7-positions (compare **4–5** and **13–15** in Table 1). As seen for **14**, the absence of dimethoxy substitution markedly affects the charge and the chemical shifts at position 1.

Interestingly, an example has been described of relationship between the methoxy group in position 6 and the reactivity of the heterocyclic part of an isoquinolinium salt: the presence of a methoxy substituent made position 1 passive for nucleophilic attack.²⁰ In contrast, no similar effect was observed for the 2-benzopyrylium salts,^{8–10} and these results provide a good experimental support for the calculations by the CNDO/2 method.

According to these calculations, the charge distribution in the heterocyclic fragment of the 2-benzopyrylium cation is determined by the substituents at C-1 and C-3. Thus, the ΣQ_{C-4} value depends mainly on the substituent in position 3 and increases considerably when R² = H (compare **1**, **3** and **2**). The influence of R¹ in this case is insubstantial. The δ value of H-4 for **2**, **3**, **5–10**, **12** and **15** increases from 6.96 to 7.63 ppm in the ¹H NMR spectra with increase in ΣQ_{C-4} from -0.136 to -0.092 (Table 1). The unique

compound **3** without a substituent in position 3 has $\delta = 7.63$ ppm and $\Sigma Q_{C-4} = -0.092$, leading to an apparent linear regression, and the following equation is given by a least-squares analysis:

$$\delta = -17.88\Sigma Q_{C-4} + 9.30 \quad (1)$$

The regression coefficient is -0.928 .

Less satisfactory relationships have been found for the series of charge densities for C-5 and C-8 and the δ values of H-5 and H-8 reported in Table 1. In these cases the regression coefficients are -0.461 and -0.636 , respectively. Obviously, this is the result of the overall effect of the methoxy, R¹ and R² substituents and the anisotropic effect of the heteroatom.²¹ Nevertheless, we have based the assignments of the H-5 and H-8 signals at 7.18–7.50 and 7.21–7.83 ppm, respectively, on the charge density values for C-5 and C-8 for salts **2**, **3**, **5–10**, **12** and **15**.

For the heterocyclic fragment of the cation, a linear correlation also exists between the charge densities on C-1 and C-3 and the chemical shifts of the methyl substituents in positions 1 and 3. Thus, when R¹ = CH₃ (**3**, **5**, **8**, **12**, **14** and **15**), the increase in the ΣQ_{C-1} value from 0.278 to 0.310 gives rise to a deshielding of the δ value of the methyl signal from 2.83 to 3.10 ppm. The unique compound **14** without a dimethoxy substituent has $\Sigma Q_{C-1} = 0.316$ and $\delta = 3.10$ ppm for 1-CH₃ methyl protons, leading to the following apparent correlation:

$$\delta = 8.33\Sigma Q_{C-1} + 0.47 \quad r = 0.866 \quad (2)$$

When R² = CH₃ (**2**, **5**, **7**, **9** and **10**), a change in ΣQ_{C-3} from 0.277 to 0.313 gives a range of δ values of 2.39–2.50 ppm (see Table 1).

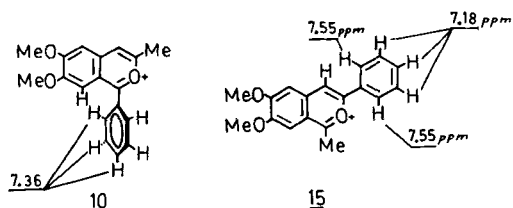
As one could expect,¹⁹ the application of standard geometry for other semi-empirical calculations by the MINDO/3 and MNDO methods* gave no satisfactory

* We did not use the AM1 method²² in this case, since there is no need to take account of the hydrogen bond parameters which are the main distinguishing feature in comparison with the MNDO method.

Table 2. Charge densities (ΣQ) of atoms C-1 to C-8 calculated by the MINDO/3 and MNDO methods with the total optimization of all geometric parameters for salts **2–5**

Compound	Method	ΣQ							
		C-1	O-2	C-3	C-4	C-5	C-6	C-7	C-8
2	MINDO/3	0.4509	-0.3170	0.4025	-0.1837	-0.2600	0.4618	0.3118	-0.1083
	MNDO	0.2525	-0.1024	0.1056	-0.0959	-0.1981	0.2965	0.1616	-0.0922
3	MINDO/3	0.4763	-0.3228	0.3708	-0.1604	-0.2554	0.4578	0.3028	-0.0952
	MNDO	0.2303	-0.1055	0.1278	-0.0988	-0.1934	0.2893	0.1641	-0.0960
4	MINDO/3	0.5098	-0.3434	0.3937	-0.1617	-0.0630	0.1207	-0.0086	0.0758
	MNDO	0.2681	-0.0972	0.0932	-0.0668	-0.0691	0.0652	-0.0422	0.0227
5	MINDO/3	0.4713	-0.3486	0.4017	-0.1837	-0.2558	0.4541	0.3153	-0.1170
	MNDO	0.2280	-0.1075	0.1085	-0.0966	-0.1966	0.2886	0.1655	-0.0989

relationships for the charge densities and the δ values of 2-benzopyrylium cations **1**–**15**. At the same time the calculations with the total optimization of all geometric parameters by the MINDO/3²³ and MNDO²⁴ methods revealed the same tendency for the charge distribution for several examples with **2**–**5**, except ΣQ_{C-1} and ΣQ_{C-3} for **2**, in comparison with the CNDO/2 method (see Tables 1 and 2). However, the data presented in Table 2 exhibit poorer relationships for the charge densities and the ¹H NMR chemical shifts in comparison with the CNDO/2 method, and especially the MNDO method. It should be noted that these facts are in good agreement with the known assessment of the application of different semi-empirical methods¹⁹ and confirm the choice of the CNDO/2 method for correlation of charge densities with ¹H NMR data for 2-benzopyrylium salts.



The phenyl-substituted salts **10** ($R^1 = \text{Ph}$, $R^2 = \text{CH}_3$) and **15** ($R^1 = \text{CH}_3$, $R^2 = \text{Ph}$) occupy a special position in the correlation between the quantum chemical calculations by the CNDO/2 method and experimental ¹H NMR data. An unusual assumption has been made in the literature for the interpretation of the ¹³C NMR spectra of 1-aryl-substituted 2-benzopyrylium salts: it has been assumed that the sp^2 hybridized atom C-1 exists in the geometry of sp^3 hybridization.¹³ As the consequence, the C-1—Ar bond is out of the plane of the cation with simultaneous rotation of the aryl substituent around this bond by 90°. The standard geometry for the CNDO/2 method assumes coplanarity for the planar cation and the aryl substituents. This is in good agreement with the ¹H NMR data for **15**, since a coplanar arrangement of the cation and the phenyl substituent is manifested by the multiplet signals of the phenyl hydrogen atoms with integral intensities in a 2 : 3 ratio. A similar observation was made for the spatial arrangement of the α -phenyl substituents in monocyclic pyrylium salts.²⁵

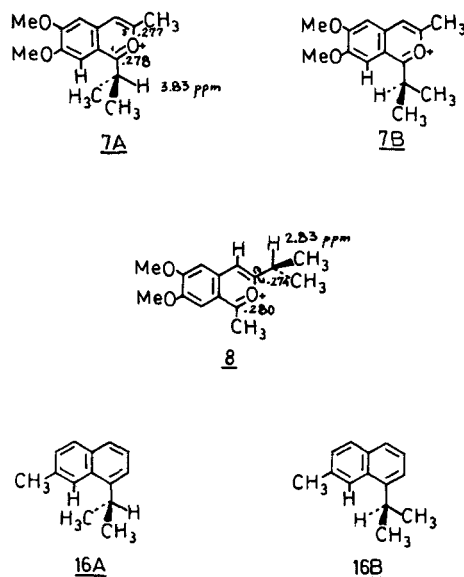
For the case of the salt **10**, the signals of the phenyl hydrogen atoms appear as one multiplet, which can be explained by the arrangement of the phenyl ring plane at C-1 at an angle to the plane of the cation.²⁵ Since this fact is not taken into account in the CNDO/2 method, an abnormally low value of $\Sigma Q_{C-8} = -0.178$ is obtained for **10**. This is why the δ value of H-8 at 7.50 ppm does not correlate with the charge density on C-8 for **10** in comparison with the other compounds (Table 1). Unfortunately, it is impossible to make a

more accurate spatial description of **10** using the ¹H NMR data.

It should be mentioned that the deshielding effect of the aryl substituent on the signal of the methyl group in another position of the heterocycle is obviously due to the ring current having greater efficacy in the approximate planar system²⁶ (compare the δ values of the 3-methyl signal at 2.40 and 2.50 ppm for **5** and **10**, respectively, and the δ values of the 1-methyl signal at 2.84, 2.93 and 3.10 ppm for **5**, **15** and **14**, respectively, in Table 1).

The hindrance of free rotation around the single bond for the bulky substituent in position 1 of the 2-benzopyrylium cation is obvious also for the salt **7**. This fact makes plausible the existence of **7** as two rotamers, **7A** and **7B**.

Recently different rotamers for the α, α' -substituted *N*-isopropylpyrylium salts have been detected by dynamic ¹H NMR spectroscopy.²⁷ The isopropyl group in 1-isopropyl-2-methylnaphthalene is preferentially locked on the *peri* hydrogen (gear effect²⁷) with rotamer **16A**, but not **16B**.²⁸



One can see the structural similarity between **16A** and **7A**. There is also an anomalous deshielding of the methine hydrogen signal of the isopropyl group for **7** (3.83 ppm) in comparison with the same signal for **8** (2.83 ppm), whereas the change in charge densities for C-1 and C-3 (CNDO/2 method) is almost zero. This result can be easily explained by the shielding of the methine hydrogen atom of the 1-isopropyl group due to the existence of **7** as the rotamer **7A**, whereas there is no hindrance for the rotation of the 3-isopropyl group in **8**.

CONCLUSION

The ^1H NMR chemical shifts of substituted 2-benzopyrylium salts are mainly in good agreement with the charge distribution in the cation calculated by the CNDO/2 method, whereas some other semi-empirical calculations (MINDO/2 and MNDO) do not give such a satisfactory correlation. On the basis of data obtained, the structural peculiarities of some 2-benzopyrylium salts can be determined.

However, the effect of the ring current and the magnetic anisotropy of the heteroatom must be taken into account for the deviations from linearity of the relationship between the proton chemical shift and the charge densities calculated by the the CNDO/2 method for the 2-benzopyrylium salts.

EXPERIMENTAL

^1H NMR spectra were recorded with a Tesla BS-487 spectrometer at 80 MHz at 20 °C. Trifluoroacetic acid was used as a solvent for all measurements; hexamethyldisiloxane was added as the lock signal for the internal stabilization.

3-Isopropyl-6,7-dimethoxy-1-methyl-2-benzopyrylium perchlorate (**8**) was obtained as described³⁰ by acylation of 1-(3,4-dimethoxyphenyl)-3-methylbutane-2-one with acetic anhydride in the presence of 70% perchloric acid (80% yield); m.p. 196 °C (from glacial acetic acid).

6,7-Dimethoxy-3-(3,4-dimethoxybenzyl)-1-methyl-2-benzopyrylium perchlorate (**12**) was obtained by acylation of α,α' -di(3,4-dimethoxyphenyl)acetone³⁴ with an equimolar amount of acetic acid in polyphosphoric ester³⁵ (70% yield); m.p. 201 °C (from glacial acetic acid).

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