# ON SOME 2,4,6-TRIPHENYLPYRIDINIUM 2-BENZIMIDAZOLATE INNER SALTS

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Molecular and electronic structure of the titled inner salts **1a–1c** is discussed on the basis of the PM3, AM1 and CNDO/2 calculations. Compounds **1a**, **1b** and **1c** were prepared from 1-(benzimidazol-2-yl)-2,6-diphenyl-4-(4-X-phenyl)pyridinium perchlorates (**2a–2c**) by chromatography on alumina only in forms of relatively stable clusters with water and solvent molecules. Mass spectra of the prepared substances are discussed.

**Key words:** Pyridinium benzimidazolates; PM3 method; Dipole moments calculation.

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Mesomeric betaines of pyridinium benzimidazolate type are of interest especially in connection with their unusual optical properties[1] and extremely high dipole moments[2]. In this communication effects of the X-substituent in 2,4,6-triphenylpyridinium 2-benzimidazolates **1a–1c** upon their molecular structure and polarity have been investigated using some semiempirical MO calculations. The results are verified by the same theoretical treatment of pyridinium 2-benzimidazolate (**3**) and 2,4,6-triphenylpyridinium 5,6-dimethyl-2-benzimidazolate (**4**) whose dipole moments and solid state structure are known[2].

## EXPERIMENTAL

All melting points were determined on a Boetius block and are uncorrected. NMR spectra were recorded on a GEMINI spectrometer at 300 MHz for $^{1}$H and at 75 MHz for $^{13}$C nuclei. The spectra were taken in $CDCl_3$ and chemical shifts (δ) are expressed in ppm values relative to inner TMS standard. In the case of solvates, the signals of all involved solvents were observable. Mass spectra were measured on a FINNIGAN MAT 90 double sector instrument of BE geometry. The elemental composition determination of all samples was carried out by the peak-matching method, using the manufacturer's software. Experimental conditions for electron impact: electron energy 70 eV, emission current 0.7 mA, ion source temperature 200 °C, DIP temperature 250–300 °C.

### Benzene–Water Cluster of 2,4,6-Triphenylpyridinium-1-(2-benzimidazolate) (**1a**)

A solution of perchlorate **2a** (ref.[3]; 1 g, 2 mmol) in chloroform (5 ml) was chromatographed on a column of alumina (100 g, II-neutral according to Brockmann) in the same solvent. Red fractions were collected and evaporated in vacuo. The residue (0.8 g, 81%) was crystallized from a benzene–heptane mixture and gave a ternary addition compound (orange crystals) of m.p. 265–267 °C. References[2,4] give m.p. 255–257 °C and 265–268 °C for compound **1a**. For $C_{30}H_{21}N_3 . C_6H_6 . H_2O$ (519.6) calculated: 83.21% C, 5.62% H, 8.09% N; found: 83.17% C, 5.69% H, 8.16% N. HR MS for $[C_{30}H_{21}N_3–H]^+$ calculated: 422.1657, measured: 422.1660. $^1$H NMR spectrum: 6.95–6.99 m, 2 H (H-4a and H-7a); 7.18–7.29 m, 6 H (*m*,*p*-Ph and *m*,*p*-Ph6); 7.40–7.44 m, 2 H (H-5a and H-6a); 7.49–7.54 m, 4 H (*o*-Ph2 and *o*-Ph6); 7.60–7.67 m, 3 H (*m*,*p*-Ph4); 7.85–7.89 m, 2 H (*o*-Ph4); 8.06 s, 2 H (H-3 and H-5). $^{13}$C NMR spectrum: 118.09 CH, 119.81 CH, 125.05 CH, 128.52 CH, 128.98 CH, 129.53 CH, 130.63 CH, 131.04 CH, 132.96 CH, 133.74 C, 134.98 C, 151.84 C, 156.67 C, 158.65 C.

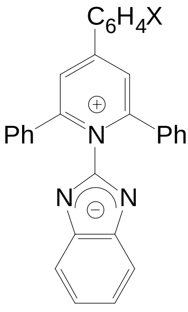
### Chloroform–Water Cluster of 4-(4-Nitrophenyl)-2,6-diphenyl-1-(2-benzimidazolate) (**1b**)

A mixture 4-(4-nitrophenyl)-2,6-diphenylpyrylium perchlorate[5] (1 g, 2.2 mmol) and 2-aminobenzimidazole (0.31 g, 2.3 mmol) and ethanol (10 ml) was stirred and refluxed for 3 h. Yellow pyridinium salt **2b** crystallized from the reaction mixture after cooling, yield 0.9 g (72%), m.p. 172–174 °C. In the HR MS for $[C_{30}H_{21}ClN_4O_6 – HClO_4]^+$ calculated: 468.1586, found: 468.1558. $^1$H NMR spectrum: 7.02–7.06 m, 2 H (H-4a and H-7a); 7.22–7.36 m, 6 H (*m*,*p*-Ph2 and *m*,*p*-Ph6); 7.40–7.44 m, 2 H (H-5a and H-6a); 7.57–7.62 m, 4 H (*o*-Ph2 and *o*-Ph6); 8.05–8.09 m, 2 H (*m*-Ph4); 8.12 s, 2 H, (H-3 and H-5); 8.46–8.50 m, 2 H (*o*-Ph4). $^{13}$C NMR spectrum: 117.98 CH, 121.04 CH, 125.61 CH, 126.07 CH, 129.24 CH, 129.67 CH, 129.93 CH, 131.56 CH, 133.56 C, 141.07 C, 143.81 C, 150.51 C, 154.84 C, 159.43 C. Work-up as decribed in the case of betaine **1a** provided 0.7 g (70%) of a red product of m.p. 228–231 °C after crystallization from chloroform. For $C_{30}H_{20}N_4O_2 . CHCl_3 . 1/2 H_2O$ (596.9) calculated: 62.37% C, 3.72% H, 9.39% N; found: 62.49% C, 3.65% H, 9.01% N. In the HR MS for $[C_{30}H_{20}N_4O_2]^{+\bullet}$ calculated: 468.1586, found: 468.1550. $^1$H NMR spectrum: 7.18–7.22 m, 2 H (H-4a and H-7a); 7.24–7.39 m, 8 H (H-5a, H-6a, *m*,*p*-Ph2, *m*,*p*-Ph6); 8.09–8.13 m, 2 H (*m*-Ph4); 8.22 s, 2 H (H-3 and H-5); 8.39–8.43 m, 2 H (*o*-Ph4). $^{13}$C NMR spectrum: 116.90 CH, 125.09 CH, 125.50 CH, 127.29 CH, 129.47 CH, 129.98 CH, 130.44 CH, 131.58 C, 132.19 CH, 140.81 C, 141.08 C, 150.64 C, 157.85 C, 159.27 C.

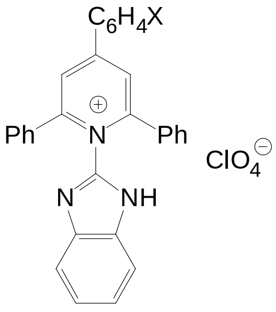
### Toluene–Water Cluster of 4-(4-Dimethylaminophenyl)-2,6-diphenylpyridinium-1-(2-benzimidazolate) (**2c**)

4-(4-Dimethylaminophenyl)-2,6-diphenylpyrylium perchlorate[6] was converted to corresponding pyridinium salt **2c** in the same way as in the case of **2b**. Yield 72% of perchlorate **2c**, m.p. 163–165 °C. In the HR MS for $[C_{32}H_{27}N_4ClO_4 – HClO_4]^+$ calculated: 466.2157, found: 466.2130. $^1$H NMR spectrum: 6.77–6.82 m, 2 H (*m*-Ph4); 6.92–6.96 m, 2 H (H-4′ and H-7′); 7.15–7.28 m, 6 H (*m*,*p*-Ph2 and *m*,*p*-Ph6); 7.38–7.42 m, 2 H (H-5′ and H-6′); 7.48–7.53 m, 4 H (*o*-PH2 and *o*-Ph6); 7.79–7.84 m, 2 H (*o*-Ph4); 7.90 s, 2 H (H-3 and H-5). $^{13}$C NMR spectrum: 40.73 $CH_3$, 113.03 CH, 117.94 CH, 119.43 CH, 120.31 C, 121.78 CH, 128.76 CH, 129.47 CH, 130.05 CH, 130.54 CH, 134.41 C, 145.57 C, 152.20 C, 153.92 C, 155.27 C, 157.37 C.

Salt **2c** (0.6 g) was chromatographed on alumina (80 g) in the same way as in the case of **2a** but using a chloroform–toluene (1 : 1) mixture as eluent. Yield 0.35 g (64%) orange crystals of inner salt **1c** melting in the region of 188–208 °C (after crystallization from a chloroform–toluene mixture). For $C_{32}H_{26}N_4 . 1/3 C_7H_8 . 5/3 H_2O$ (527.3) calculated: 78.20% C, 6.11% H, 10.62% N; found: 78.26% C, 5.77% H, 10.48% N. In the HR MS for $[C_{32}H_{26}N_4]^{+\bullet}$ calculated: 466.2157, measured: 466.2130. $^1$H NMR spectrum: 6.47–6.79 m, 2 H (*m*-Ph4); 7.10–7.14 m, 2 H (H-4a and H-7a); 7.19–7.28 m, 6 H (*m*,*p*-Ph2, *m*,*p*-Ph6; 7.34–7.38 m, 2 H (H-5a and H-6a); 7.54–7.59 m, 4 H (*o*-Ph2 and *o*-Ph6); 7.81–7.85 m, 2 H (*o*-Ph4); 7.89 s, 2 H (H-3 and H-5). $^{13}$C NMR spectrum: 40.76 $CH_3$, 113.16 CH, 116.91 CH, 119.62 C, 121.70 CH, 123.91 CH, 129.17 CH, 129.69 CH, 131.09 CH, 131.22 CH, 132.93 C, 137.93 C, 143.03 C, 154.71 C, 156.70 C, 157.22 C.

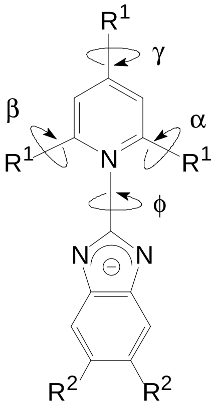


**1**



**2**

| **1,2** | X |
|---|---|
| **a** | H |
| **b** | 4-$NO_2$ |
| **c** | 4-$NMe_2$ |



| | $R^1$ | $R^2$ |
|---|---|---|
| **3** | H | H |
| **4** | Ph | Me |

## RESULTS AND DISCUSSION

Preparation of compounds **1a–1c** from corresponding X-substituted 2,4,6-triphenylpyridinium perchlorates **2a–2c** was attempted by a novel chromatographic procedure using basic alumina. Previously reported preparations of betaine **1a** are based on the perchloric acid elimination from perchlorate **2a** by potassium hydroxide[7] or by an anionic (hydroxide form) ion exchange resin[2]. We have found out that product melting at 265–267 °C is not a pure inner salt **1a** but a cluster of composition **1a**–$C_6H_6$–$H_2O$. Our attempts to remove the solvent components by heating in vacuo without decomposition of the substance have been unsuccessful but the presence of ion [**1a** – H]$^+$ at 200 °C was proved by high resolution mass spectrometry (HR MS). It may be noted that in previous studies the inner salt has been reported to be either a monohydrate melting at 149–150 °C (after crystallization from benzene)[7] or no elemental analyses supporting composition of the higher melting form have been given[2,4]. Similarly, compound **4** has been reported[2] to form a dihydrate with disordered water molecules.

Attempts at the preparation of new inner salts, namely 4-(4-nitrophenyl)-2,6-diphenyl-1-(2-benzimidazolate) (**1b**) with the π-electron withdrawing 4-nitro group as well as 4-(4-dimethylaminophenyl)-2,6-diphenylpyridinium-1-(2-benzimidazolate) (**1c**) with the π-electron releasing 4-dimethylamino group, have resulted only in clusters of the approximate compositions 2 **1b**–2 $CHCl_3$–$H_2O$ and 3 **1c**–toluene–5 $H_2O$, respectively. The high solvent affinity of inner salts **1b** and **1c** require some corrections in any quantitative interpretation of their optical properties[1].

Mass spectrometric fragmentation of inner salts **1a–1c** has been observed to take place at the benzimidazolate part of the molecules. Thus, $[M^\bullet]^+$ radical cations from betaines **1b**, **1c** are identical with $[M - HClO_4^\bullet]^+$ ionic species from perchlorates **2b**, **2c** and the processes may be written by the Eq. (*1*):

$$\mathbf{1} - e \rightarrow [M^\bullet]^+ \leftarrow \mathbf{2} - HClO_4 - e \quad . \qquad (1)$$

High resolution mass analyses have proved this conclusion.

The standard PM3 procedure[8] was used for the molecular geometry optimization of inner salts **1a**, **1b**, **1c**, **3** and **4**. To check reliability of the semiempirical approach comparison of some X-ray determined[2] bond lengths and appropriate PM3 atom–atom distances have been investigated (Table I). It may be claimed a satisfactory agreement between the theoretical and experimental quantities except of some five-membered ring bonds (N1′–C2′, N1′–C7′a and C2′–N3′).

Heats of formation for the optimized structures **1a**, **1b**, **1c**, **3** and **4** were calculated to be 192.0, 186.1, 187.4, 109.3 and 174.8 kcal/mol, respectively.

It may be expected that torsional angles between the planes of neighbouring π-subsystems (α, β, γ, and ϕ) gives the best picture of general molecular shapes of studied inner salts. It follows from Table II that only the parent molecule **3** is predicted to be planar in agreement with its X-ray structure[2]. On the other hand, the α, β and ϕ values for the non-planar molecule **4** agree with its quasi-perpendicular molecular X-ray structure[2]. Considering the predicted torsional angles for compounds **1a**, **1b** and **1c** (Table II) one may conclude a little effect of the 4-dimethylamino group contrary to a significant influence of the π-electron withdrawing 4-nitro group. However, coplanarity of the 4-aryl and pyridine rings is conserved in all cases thus showing importance of π-overlaps between the rings. The dipole moments of the inner salts **1a**, **3** and **4** have been reported[2] to be 13.08, 10.33 and even 18.70 D, respectively, which may correspond to the value of 11.06 D calculated[2] for compound **3** by the MNDO method. Dipole moments for all studied inner salts calculated by the CNDO/2, AM1 and PM3 methods are given in Table III. The values of μ document that all inner salts **1a**, **1b**, **1c**, **3** and **4** should be

TABLE I
Selected bond lengths (Å) observed and calculated for inner salts **3** and **4**

| Bond | Compound **3** | | Compound **4** | |
|---|---|---|---|---|
| | X-Ray[a] | PM3 | X-Ray[a] | PM3 |
| N1–C2 | 1.33 | 1.38 | 1.36 | 1.38 |
| N1–C6 | 1.38 | 1.38 | 1.37 | 1.38 |
| N1–C2′ | 1.45 | 1.40 | 1.49 | 1.44 |
| C2–C3 | 1.37 | 1.39 | 1.39 | 1.40 |
| C3–C4 | 1.37 | 1.39 | 1.40 | 1.40 |
| C4–C5 | 1.38 | 1.39 | 1.41 | 1.40 |
| C5–C6 | 1.39 | 1.39 | 1.40 | 1.39 |
| N1′–C2′ | 1.30 | 1.40 | 1.43 | 1.38 |
| N1′–C7′a | 1.42 | 1.37 | 1.40 | 1.39 |
| C2′–N3′ | 1.35 | 1.40 | 1.33 | 1.38 |
| N3′–C3′a | 1.33 | 1.37 | 1.39 | 1.39 |
| C3′a–C4′ | 1.42 | 1.42 | 1.38 | 1.41 |
| C3′a–C7′a | 1.42 | 1.44 | 1.44 | 1.43 |
| C4′–C5′ | 1.36 | 1.37 | 1.39 | 1.38 |
| C5′–C6′ | 1.39 | 1.43 | 1.41 | 1.43 |
| C6′–C7′ | 1.38 | 1.37 | 1.36 | 1.38 |
| C7′–C7′a | 1.39 | 1.42 | 1.37 | 1.41 |

[a] Taken from ref.[2].

very polar substances. However, it seems necessary that the reported[2] $\mu_{exp}$ values have to be considered with caution because of the stable cluster formation. Only the excellent agreement between the experimental moment $\mu_{exp}$ = 10.33 D for unsubstituted compound **3** with the value $\mu$ = 10.34 D calculated by the CNDO/2 method may be regarded as a correct reliability verification of the semiempirical procedure. On the other hand, the apparent moments $\mu_{exp}$ = 13.08 and 18.70 D of compounds **1a** and **4** are hardly comparable with the calculated values $\mu$ = 14.40 and 13.74 D since the Halverstadt–Kumler extrapolation method[9] is probably not able to eliminate effects of strongly

TABLE II
Torsional angles between some molecular fragments in studied inner salts calculated by the PM3 method[a]

| Compound | Angle[b], ° | | | |
|---|---|---|---|---|
| | $\alpha$ | $\beta$ | $\gamma$ | $\phi$ |
| **1a** | 97.5 | 96.9 | 0.0 | 94.8 |
| **1b** | 71.7 | 73.2 | 0.0 | 72.7 |
| **1c** | 97.3 | 97.7 | 0.0 | 94.9 |
| **3** | – | – | – | 0.0 |
| **4** | 98.6 | 95.3 | 0.0 | 94.5 |

[a] See formulae **3**, **4**; [b] X-substituent is coplanar with the aromatic ring.

TABLE III
Calculated dipole moment (in debyes) of studied inner salts

| Compound | ($\mu_{exp}$) | Calculated $\mu$-values | | |
|---|---|---|---|---|
| | | CNDO/2 | AM1 | PM3 |
| **1a** | (13.08)[a] | 14.40 | 10.94 | 11.36 |
| **1b** | | 7.44 | 4.23 | 4.71 |
| **1c** | | 16.00 | 13.89 | 16.00 |
| **3** | (10.33)[a] | 10.34[b] | 8.66 | 7.71 |
| **4** | (18.70)[a] | 13.74 | 10.67 | 11.08 |

[a] Experimental value (in dioxane) reported in ref.[2]; [b] MNDO calculated value 11.06 D, see ref.[2].

bound solvent (dioxane, water) molecules upon total polarization of the samples. Especially the unusually high dipole moment[2] 18.70 D appears to be incorrect in relation to the real molecular and electronic structures of free betaine **4**. In addition, the data given in Table III all predict dipole moments for dimethyl derivative **4** to be lower than those for non-methylated compound **1a**.

As expected, the π-electron releasing 4-dimethylamino group in inner salt **1c** enhances the dipole moment with respect to that in unsubstituted compound **1a** by 1.60–1.95 D contrary to the effect of the π-electron withdrawing 4-nitro group in betaine **1b** for which a significant decrease by 6.30–6.44 D is predicted.

Considering carbon and nitrogen centres in the PM3 models of all studied molecules, it can be seen that only the N1 centres are positively charged. Charge densities at selected atomic centres at connection between the both heterocyclic systems of compounds **1a**, **1b**, **1c** and **3** are presented in Table IV. The presence of the 2,4,6-aryl groups causes an increase of all followed charges, except the positions C2′ and C6′. The effect of the different π-electron affinities of the X-groups far from the selected positions is still perceptible. Provided the charge difference $\Delta Q(\mathrm{N1,C2'}) = Q(\mathrm{N1}) - Q(\mathrm{C2'})$ is chosen as a measure of the N1–C2′ bond polarity, one can see that the charge separation is kept down just in the planar molecule **3** due to π-delocalization between the two heterocyclic ring systems. In agreement with this interpretation, the calculated N1–C2′ bond length for the planar inner salt **3** is shorter (1.40 Å) than those in orthogonally shaped salts **1a**, **1b** and **1c** (1.44, 1.43 and 1.44 Å, respectively). As expected, the $Q(\mathrm{N1,C2'})$ values (Table IV) exhibit opposite relationships.

TABLE IV
Charge densities at selected atomic centres of inner salts **1a–1c** and **3** calculated by the PM3 method

| Compound | $Q$(N1) | $Q$(C2) | $Q$(N1′) | $Q$(C2′) | $\Delta Q$(N1,C2′) |
|---|---|---|---|---|---|
| **1a** | +0.743 | –0.096 | –0.176 | –0.346 | 1.089 |
| **1b** | +0.763 | –0.102 | –0.166 | –0.365 | 1.128 |
| **1c** | +0.734 | –0.096 | –0.177 | –0.341 | 1.078 |
| **3** | +0.812 | –0.289 | –0.131 | –0.406 | 0.943 |

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