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# Synthesis and crystal structure determination of 2,6-di-*tert*-butyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate and its corresponding perchlorate salt

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## ABSTRACT

2,6-Di-*tert*-butyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate belongs to the class of negatively solvatochromic dyes commonly used for the empirical determination of solvent polarities. By way of exception, it crystallizes without any solvent of crystallization due to the presence of two bulky *tert*-butyl groups in the phenolate moiety. The synthesis of this hydrophobic betaine dye has been improved and an X-ray crystal structure analysis of this solventless zwitterionic dye and its protonated form (as a perchlorate salt) has been carried out.

## 1. Introduction

Pyridinium-*N*-phenolate betaine dyes belong to the most widely used class of *functional dyes* [1] because of their pronounced negative solvatochromism (perichromism), i.e., hypsochromic shift of the long-wavelength visible absorption band with increasing polarity of the surrounding solvent (environment). The extreme negative solvatochromism of the standard betaine dye 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (**1**, Fig. 1) has been used to introduce an empirical scale of solvent polarity, $E_T(30)$ [2,3]; the corresponding normalized scale is called $E_T^N$ scale [2b].

The standard betaine dye **1** has been used to characterize the polarity of traditional molecular solvents [2,3], and also that of ionic liquids [4], various types of organized solutions [3b,3d,5], including supramolecular systems [3b,6], as well as liquid/liquid, solid/liquid, and solid/air interfaces [7]. In addition, the unique spectral sensitivity of **1** has been used to examine the nature of microenvironments in nano-dispersed systems [8]. Because of their basic phenolate moiety, these betaine dyes can be easily and reversibly protonated, with disappearance of the solvatochromic visible absorption band as a consequence. That is, pyridinium-*N*-phenolate betaine dyes are in fact combined solvatochromic and acid/base indicators [5e,9].

Consequently, not only highly dipolar zwitterionic betaine dyes $D^{\pm}$, but also their corresponding protonated colorless cationic species $HD^{+}$ can participate in the formation of the desired analytical signal. Therefore, it is of significance to shed light on the changes in molecular structure connected with the protonation of these betaine dyes. This is of particular interest for such investigations in which the betaine indicator is embedded into thin interfacial regions such as the Stern layer of micelles formed by ionic surfactants.

The standard betaine dye **1** always crystallizes with some solvent of crystallization and is not available in an anhydrous form. An anhydrous betaine dye was particularly necessary for the determination of the ground- and excited-state dipole moment of such zwitterionic betaine dyes [10,11]. For this reason, the two 2,6-phenyl groups of **1** were replaced by two sterically more demanding *tert*-butyl groups, in order to prevent hydrogen-bonding of the phenolate oxygen atom with the hydrogen-bond donor (HBD) solvents commonly used for the recrystallization of these betaine dyes.

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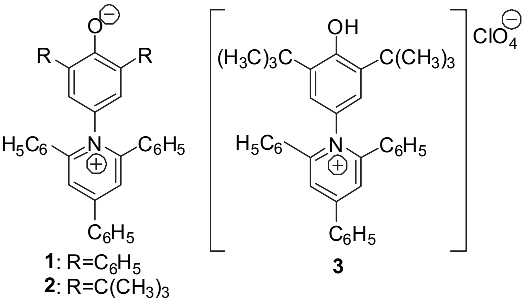


**Fig. 1.** Molecular structure of pyridinium-*N*-phenolate betaine dyes **1**, **2** and the perchlorate salt **3**.

This 2,6-di-*tert*-butyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (**2**) crystallizes without any solvent of crystallization, and is now even soluble in nonpolar solvents such as cyclohexane, but no longer soluble in water. Because of its solubility in apolar solvents (i.e., solvents without own permanent dipole moment), it has been used to determine its ground-state permanent dipole moment ($\mu_g$ = 14.8 ± 1.2 D in 1,4-dioxane [10,11]). For the excited-state dipole moment of **2** ($\mu_e$ = 6.2 ± 0.3 D in 1,4-dioxane) changes its direction [11,12].

In order to evaluate the steric shielding of the phenolate part of this di-*tert*-butyl-substituted betaine dye, an X-ray diffraction study of the starting perchlorate **3** and betaine dye **2** has been carried out; X-ray crystal structure determinations of other pyridinium-*N*-phenolate betaine dyes have been reported [13a–13d]. In contrast to **2**, the *N*-(4-hydroxyphenyl)pyridinium salt **3** crystallizes with one water molecule per unit cell.

Because of the usefulness of the hydrophobic solvent-free betaine dye **2**, its synthesis has been improved (Scheme 1 and Experimental section). The negative solvatochromism of **2** is with $\lambda_{max}$ = 918 (in cyclohexane) and 582 nm (in formamide) → $\Delta\lambda = -336$ nm [2a,14] nearly as large as that of the standard betaine dye **1**. The $E_T(2)$ values (in kcal/mol) correlate linearly with $E_T(1)$ [ = $E_T(30)$] values: $E_T(2) = 0.781 \cdot E_T(30) + 4.94$ ($n = 47$; $r = 0.943$) [14].

## 2. Results and discussion

An improved version of the four-step synthesis of betaine dye **3**, first given in reference [2a], is described in Scheme 1: Nitrosation of commercially available 2,6-di-*tert*-butylphenol **4** gave the tautomeric 2,6-di-*tert*-butyl-1,4-benzoquinone-4-monoxime **5**. Palladium-catalyzed reduction of **5** with dihydrogen at normal pressure yielded the oxygen-sensitive 4-aminophenol **6**, which was immediately reacted with 2,4,6-triphenylpyrylium perchlorate to give *N*-(4-hydroxyphenyl)pyridinium salt **3**. Deprotonation of **3** with sodium methanolate in methanol gave betaine dye **2** as glittering black-green crystals, without any solvent of crystallization.

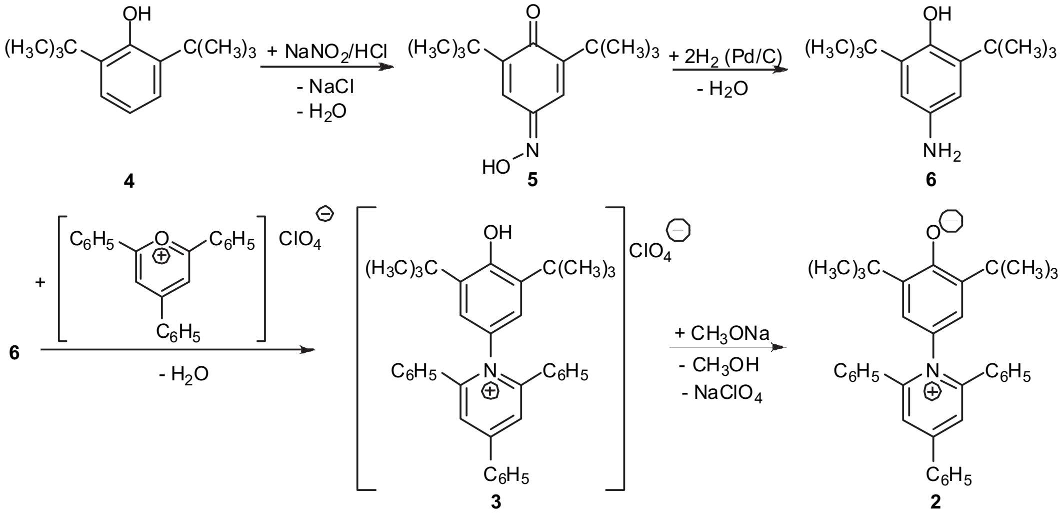
**Table 1**
Torsion angles in **3** and **2** in Å.

| Torsion angles | 3 | 2 |
|---|---|---|
| C(3)–N(1)–C(24)–C(29) | 119.1 (3) | 122.7 (3) |
| C(2)–C(1)–C(6)–C(11) | 152.2 (3) | 164.2 (3) |
| N(1)–C(3)–C(18)–C(19) | 135.0 (3) | 125.1 (3) |
| N(1)–C(4)–C(12)–C(13) | 124.8 (3) | 135.7 (3) |

Both the organic cation of **3** and the betaine dye **2** contain bulky phenyl and 2,6-di-*tert*-butyl-4-hydroxyphenyl groups which are rotated with respect to the plane of the pyridinium ring due to their mutual repulsion. Thereafter, the vicinal aryl-substituted at N(1), C(3), and C(4) are much more twisted out of plane than the phenyl group at C(1) (Table 1). However, this repulsion is counteracted by the tendency to coplanarity due to π–π conjugation between all aromatic rings which results in the occurrence of many shortened intramolecular H...H, C...H, and C...C contacts. The presence of two vicinal *tert*-butyl groups next to the hydroxyl group in **3** and the phenolate oxygen in **2** causes many shortened weak intramolecular contacts with these oxygen atoms. Most of these contacts are probably attractive (Table 2).

Because perchlorate **3**, contrary to zwitterion **2**, crystallizes with one molecule of water, it is appropriate to compare the X-ray structure data of **3** with that obtained for the protonated form of standard dye **1** by Ratajczak et al. [16]. In the crystal lattice of perchlorate **3** the water molecule is located rather far away from its phenolic OH group, without intermolecular H-bond formation. This confirms the steric shielding of the OH group by the two voluminous *tert*-butyl groups of **3**. This is in contrast to the protonated form of **1** (isolated as nitrate), for which intermolecular H-bonds between its OH group and the oxygen of the water of crystallization are registered (O–H···O bond length = 1.67 Å [16]) (Fig. 1).

It should also be noted that the geometry of the zwitterionic dye **2** does not undergo substantial changes during the protonation of **2** to give **3** (compare Figs. 2 and 3). The length of the C–O bond in **3** and **2** is typical for *ortho*-substituted phenols and the



**Scheme 1.** Synthesis of betaine dye **2** and its perchlorate salt **3** [2a,14].

**Table 2**
Shortened intramolecular contacts in **3** and **2** in Å[a].

| Contact | **3** | **2** |
|---|---|---|
| O(1)…H(31B) | 2.46 | 2.37 |
| O(1)…H(35A) | 2.27 | 2.35 |
| O(1)…H(36A) | 2.41 | 2.31 |
| O(1)…C(35) | 2.905 | |
| H(29)…H(37C) | 2.08 | 2.17 |
| H(29)…H(37B) | 2.26 | 2.10 |
| H(25)…H(33C) | 2.15 | 2.06 |
| H(25)…H(33B) | 2.21 | 2.12 |
| H(2)…H(7) | 2.24 | 1.97 |
| H(5)…H(11) | 2.24 | 2.02 |
| C(7)…H(2) | 2.71 | 2.62 |
| C(2)…H(7) | 2.66 | 2.63 |
| C(5)…H(11) | 2.74 | 2.62 |
| C(11)…H(5) | 2.69 | 2.59 |
| H(5)…C(13) | 2.88 | 2.73 |
| H(13)…C(5) | | 2.79 |
| H(2)…C(19) | 2.77 | |
| H(19)…C(2) | 2.81 | |
| C(23)…C(24) | 2.978 | 3.00 |
| C(17)…C(24) | 3.073 | 2.95 |
| C(18)…C(25) | 3.112 | 2.99 |

[a] Sum of the van-der-Waals radii [15]: O…H 2.46 Å, O…C 3.00 Å, H…H 2.34 Å, C…H 2.88 Å, C…C 3.42 Å.

corresponding phenolate ions, respectively: the C(27)–O(1) phenolate bond of **2** (1.282(4) Å) is considerably shorter than the analogous bond in cation **3** (1.371(4) Å). The first bond length is close to the typical values for *ortho*, *ortho*-disubstituted phenolate ions, i.e., 1.299 Å [17], and the second one is close to the mean value found for *ortho*, *ortho*-disubstituted phenols, i.e., 1.374 [17].

It is noteworthy that the base strength of **2** in solution dramatically exceeds that of **1**. For instance, their protonation constants differ by 1.7 logarithmic units measured in methanol [18] and by 1.8 units in a benzene/ethanol/water mixture (mass ratio 47:47:6) [18]; in microemulsions based on cationic and anionic surfactants, the corresponding differences are 1.5 and 2.3 logarithmic units, respectively [9b]. Such large differences are also observed for other 2,6-di-*tert*-butylphenols [19].

An additional factor in accordance with such effects is the shortening of the bond lengths C(27)–C(28) and C(26)–C(27) on going from **2** to **3** (Table 3). Such bond shortenings are generally observed for substituted phenolate ions (mean bond length 1.438 Å [17]), but with two bulky *ortho*-substituents the steric shielding of the phenolate moiety increases drastically. As result, both the proton transfer from the phenolic OH group to a solvent molecule and the stabilizing solvation of the corresponding phenolate ion should be hindered. In the interaction of betaine dyes with lanthanide/dipivaloylmethane complexes in acetone, dye **2** also appears as a stronger base as compared with **1** [20].

The bonds between the aromatic rings in **2**, i.e., C(1)–C(6), C(3)–C(18), C(4)–C(12), and N(1)–C(24), are slightly elongated as compared to the corresponding bonds in **3** and to the mean bond lengths of 1.487 and 1.431 Å [21], respectively (Table 3). The interplanar angles between the aromatic rings in **2** and **3** are very close to each other. Only a small decrease of the angle between the pyridinium and the phenolate ring at C(1) is observed in **2** as compared to **3**, i.e., 152.2(3)° and 164.2(3)°, respectively (Table 1). This is accompanied by an elongation of the C(1)–C(6) bond in both cases. The interplanar angle between the pyridinium and the phenolate ring in **2** (122.7(3)°) is large enough to nearly cut off the

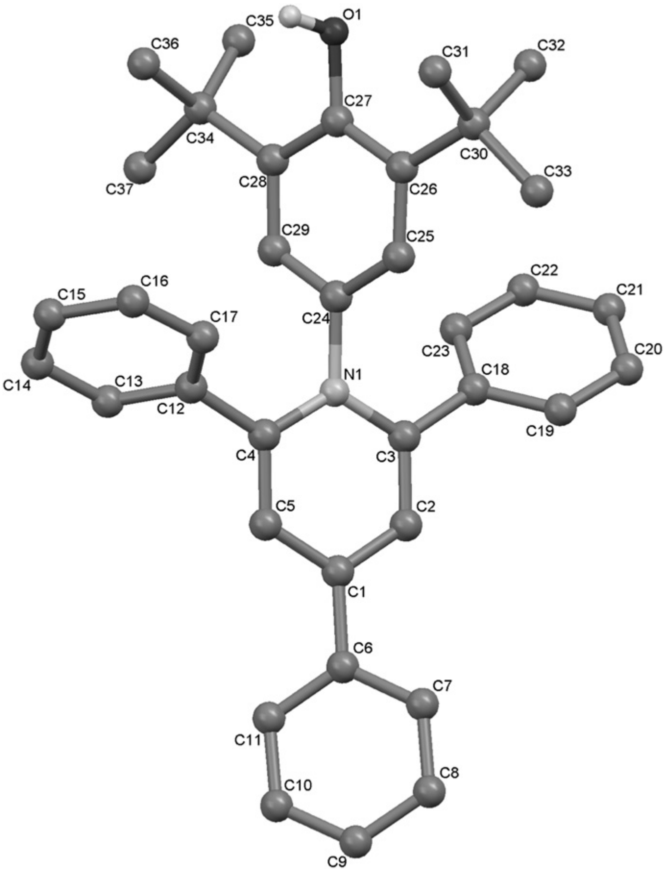


**Fig. 2.** Perspective view of the cation of **3** with atom numbering. All H- atoms except that of the hydroxy group are omitted for clarity.

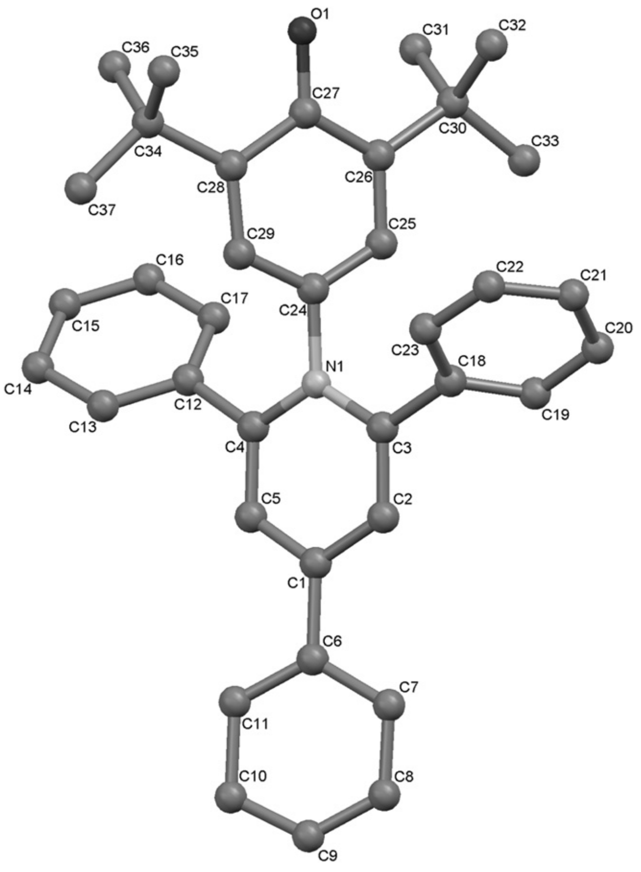


**Fig. 3.** Perspective view of betaine dye **2** with atom numbering. All H- atoms are omitted for clarity.

**Table 3**
Selected bond lengths for **3** and **2**.

| Bond | **3** | **2** |
|---|---|---|
| O(1)–C(27) | 1.371 (4) | 1.282 (4) |
| N(1)–C(24) | 1.463 (4) | 1.482 (4) |
| C(3)–C(18) | 1.475 (4) | 1.493 (4) |
| C(4)–C(12) | 1.480 (4) | 1.509 (4) |
| C(1)–C(6) | 1.482 (4) | 1.500 (4) |
| C(1)–C(2) | 1.381 (4) | 1.399 (4) |
| C(2)–C(3) | 1.363 (4) | 1.387 (4) |
| C(3)–N(1) | 1.377 (4) | 1.383 (4) |
| N(1)–C(4) | 1.371 (4) | 1.360 (4) |
| C(4)–C(5) | 1.370 (4) | 1.390 (4) |
| C(5)–C(1) | 1.384 (4) | 1.393 (4) |
| C(24)–C(25) | 1.372 (4) | 1.365 (4) |
| C(25)–C(26) | 1.379 (4) | 1.376 (4) |
| C(26)–C(27) | 1.407 (4) | 1.445 (4) |
| C(27)–C(28) | 1.402 (4) | 1.472 (4) |
| C(28)–C(29) | 1.387 (4) | 1.377 (4) |
| C(29)–C(24) | 1.373 (4) | 1.383 (4) |

**Table 4**
Crystallographic data parameters of data collection, structure solution, and refinement for crystal structure of perchlorate.

| | **3** | **2** |
|---|---|---|
| Crystal data | | |
| Empirical formula | $[C_{37}H_{38}NO]ClO_4 \cdot H_2O$ | $C_{37}N_{37}NO$ |
| $M_r$, g/mol | 630.15 | 511.7 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ |
| $a$, Å | 10.019 (3) | 15.796 (5) |
| $b$, Å | 21.087 (6) | 15.002 (4) |
| $c$, Å | 16.026 (4) | 12.760 (4) |
| $\beta$, ° | 96.58 (2) | 94.33(2) |
| $V$, Å$^3$ | 3364 | 3015 |
| $Z$ | 4 | 4 |
| Calculated density, $Vc$/mg m$^{-3}$ | 1.244 | 1.566 |
| $\mu$ (Mo$K\alpha$), mm$^{-1}$ | 0.160 | 0.157 |
| $T$, K | 293 | 298 |
| Data collection | | |
| $F$(000) | 1336 | 1332 |
| Independent Reflections | 5878 | 4092 |
| $R_{int}$ | 0.033 | 0.045 |
| $2\theta_{max}$, ° | 50 | 50 |
| Refinement | | |
| Reflections with $F > 4\sigma(F)$ | 2764 | 2677 |
| $R_1$ $[F^2 > 2\sigma(F^2)]$ | 0.057 | 0.043 |
| w$R_2$ (all data) | 0.167 | 0.153 |
| $S$ (goodness-of-fit) | 0.86 | 0.97 |

conjugation between the π-systems of both rings, thus confirming the zwitterionic nature of this betaine dye (Table 4).

## 3. Conclusions

The solvatochromic di-*tert*-butyl-substituted betaine dye **2** crystallizes unexpectedly without any solvent (e.g., water) of crystallization, in contrast to all other betaine dyes known [2,13], due to steric shielding of the usually H-bond accepting phenolate oxygen atom. This made it possible to determine experimentally the dipole moment of **2** as representative of all other betaine dyes. The perchlorate **3** (as protonated form of **2**) crystallizes with one water molecule per unit cell, however, the water molecule is located far away from the phenolic OH group without forming an intermolecular $H_2O \cdots H{-}O$ bond, thus also confirming the steric shielding of the OH group in **3**.

Protonation of **2** to give **3** only marginally changes the geometry of the molecule, the bond lengths of which are in good agreement with that of other *ortho*, *ortho*-disubstituted phenolates and phenols, respectively.

The elongation of the C(26)–C(27) and C(27)–C(28) bonds on going from **3** to **2** is in accord with the much stronger basicity of betaine dye **2** in solution, as compared to that of other pyridinium-*N*-phenolate betaine dyes. The large interplanar angle between the pyridinium and phenolate ring in **2** prevents π–π-conjugation between the two π-systems and confirms the zwitterionic nature of this betaine dye.

## 4. Experimental section

General: melting points (not corrected): Kofler Mikroheiztisch (Reichert) – IR spectra: Interferometer IFS 88 (Bruker) with KBr discs. – $^1$H and $^{13}$C NMR spectra: Spectrometers ARX-200 and AC-300 (Bruker). – Mass spectra: MAT 711 (Varian) with field desorption (FD). – UV/Visible spectra: UV/Visible/NIR spectrophotometer U-3410 (Hitachi) and DK-2 (Beckman), with 1.00-cm Suprasil (Hellma) quartz cells. – Elemental analyses: CHN-Automat Rapid (Heraeus) at the Analytik-Servicelabor of the Department of Chemistry, Marburg, and Microanalytical Laboratory Bernhardt, Mülheim/Ruhr. – Solvents: Solvents for synthetic work were purified according to usual standard methods. Solvents for UV/Visible spectroscopic measurements were used in the highest quality commercially available (analytical or spectroscopical grade) and were additional dried and purified by means of molecular sieves and, if necessary, by filtration through a column of basic aluminium oxide (B-Super I) in order to remove traces of acids. The solvents must be free of water and, in addition, absolutely acid-free because the betaine dye is easily protonated at the phenolate oxygen atom, with disappearance of the long-wavelength solvatochromic visible absorption band as consequence.

Data collection was performed with an automatic four-circles Siemens P3/PC for **3**, and an STOE diffractometer for **2** (graphite monochromator, Mo$K\alpha$ radiation, $\theta/2\theta$ – scans). Both structures were solved by direct methods. Structure of **2** was refined using the program system MULTAN [22]. All non-hydrogen atoms were refined in anisotropic approximation, all H- atoms were refined isotropically. Structure of **3** was refined on $F^2$ by full-matrix least squares procedure with the SHELX-97 program package [23]. All non-hydrogen atoms were refined in anisotropic approximation. H- atom positions were located geometrically and refined using the riding-model with $U_{iso} = nU_{eq}$ of the carrier atom ($n = 1.5$ for H- atoms of hydroxyl and methyl groups and 1.2 for the others H- atoms). Bond lengths O–H and distances H…H in the water molecule were constrained to 0.880(1) Å and 1.410(5) Å, respectively.

Additional material comprising atomic coordinates, anisotropic thermal parameters, full bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 808911 (**2**) and CCDC 808908 (**3**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

### 4.1. Synthesis of betaine 2 and its phenolate salt 3 [2a,14]

#### 4.1.1. 2,6-Di-tert-butylcyclohexa-2,5-dien-1,4-dione-4-oxime (5)

Following the procedure of Kharasch et al. [24], to a solution of 2,6-di-*tert*-butylphenol (**4**) (from Sigma–Aldrich) in ethanol and conc. hydrochloric acid was added an aqueous solution of sodium nitrite at −5 °C, to give, after work up and twofold recrystallization from cyclohexane, oxime **5** (81%) as yellow plates with m.p. 220–221 °C (ref. [19] 221–222 °C). – IR (KBr): $\nu$/cm$^{-1}$ = 3320 (OH), 1610 (C=O), 1008 (N–O).– $^1$H NMR ($CD_3COCD_3$): $\delta$/ppm = 1.21 (s, 9H, CMe$_3$), 1.22 (s, 9H, CMe$_3$), 6.93 (d, $^4J$ = 2.4 Hz, 1H, 3-H), 7.52

(d, $^4J$ = 2.5 Hz, 1H, 5-H), 12.1 (s, 1H, OH). – $^{13}$C NMR ($CD_3COCD_3$): $\delta$/ppm = 29.7 and 29.8 ($CH_3$), 35.7 and 36.4 ($CMe_3$), 117.9 (C-3), 131.4 (C-5), 150.0 (C-2), 150.7 (C=NOH), 152.3 (C-6), 187.8 (C=O). – MS (FD): $m/z$ (%) = 235 (100) [M+]. – $C_{14}H_{21}NO_2$ (235.3): calcd. C 71.47, H 9.00, N 5.95; found C 71.57, H 8.89, N 5.93.

#### 4.1.2. *4-Amino-2,6-di-tert-butylphenol (**6**)*

A suspension of the palladium catalyst (10 cg/g Pd on charcoal, ca. 200 mg) in a solution of **5** (4.71 g, 21.3 mmol) in anhydrous ethanol (150 mL) was reduced with dihydrogen at room temperature and normal pressure in a hydrogenation apparatus until the necessary amount of dihydrogen was absorbed. The catalyst was filtered off with a reversed fritted glass filter under nitrogen and washed with ethanol. From the combined ethanolic solutions the solvent was removed by distillation and the residue was triturated with petroleum ether (b.p. 40–60 °C). The solid was collected by filtration, washed with petroleum ether, and dried in vacuo. Reducing the mother liquor to a smaller volume gave a second crop of product. Combined yield of **6** (3.55 g; 80%) was obtained as rosa-coloured crystals of m.p. 110–112 °C (ref. [25] 108–112 °C; ref. [26] 114–116 °C), which easily oxidise on contact with air to a dark red product and should either be stored under nitrogen or immediately converted into the pyridinium salt **3**. – IR (KBr): $\nu$/cm$^{-1}$ = 3325 ($NH_2$), 1602 ($NH_2$). – $^1$H NMR ($CDCl_3$): $\delta$/ppm = 1.40 (s, 18H, $CH_3$), 3.21 (2H, $NH_2$), 4.62 (s, 1H, OH), 6.56 (s, 2H, 3-H, 5-H). – $^{13}$C NMR ($CDCl_3$): $\delta$/ppm = 30.2 ($CH_3$), 34.3 ($CMe_3$), 112.5 (C-3, C-5), 137.3 (C-2, C-6), 138.4 (C–$NH_2$), 146.6 (C–OH). – MS (FD): $m/z$ (%) = 221 (100) [M+], 206 (62) [M+ –NH or $CH_3$]. – $C_{14}H_{23}NO$ (221.3): calcd. C 75.97, H 10.47, N 6.33; found C 76.13, H 10.68, N 6.32.

#### 4.1.3. *1-[(3,5-Di-tert-butyl-4-hydroxy)phenyl]-2,4,6-triphenylpyridinium perchlorate (**3**) [2a]*

A solution of freshly prepared 4-amino-2,6-di-*tert*-butyl-4-aminophenol **6** (5.0 g, 22.6 mmol), 2,4,6-triphenylpyrylium perchlorate [27] (10.2 g, 25.0 mmol), and anhydrous sodium acetate (3.0 g) in dry ethanol (120 mL) was heated under nitrogen for 2.5 h under reflux. The hot solution was filtered and, after cooling to room temperature, acidified by addition of some aqueous perchloric acid (70 cg/g; ca. 3 mL). The precipitate formed was collected by filtration, washed acid-free with water, and dried with $P_4O_{10}$ in vacuo. After twofold recrystallization from dry ethanol, perchlorate **3** was obtained as greenish-yellow needles (6.9 g; 50%) with m.p. 244–245 °C. – UV/Visible ($CH_3OH$): $\lambda_{max}$/nm ($\varepsilon_{max}$) = 305 (34 700). – $[C_{37}H_{38}NO]ClO_4$ (612.2): calcd. C 72.60, H 6.26, N 2.29; found C 72.37, H 6.28, N 2.44. – The corresponding tetrafluoroborate can be obtained by using 2,4,6-triphenylpyrylium tetrafluoroborate [28,29] (m.p. 255–257 °C) as the starting compound. Perchlorate **3** used for its X-ray structure determination was prepared by addition of aqueous perchloric acid to a solution of betaine dye **2** in ethanol and was recrystallized from ethanol/water (1:1) to give a monohydrate of **3**.

#### 4.1.4. *2,6-Di-tert-butyl-4-(2,4,6-triphenylpyridinium-1-yl) phenolate (**2**) [2a,14]*

To a stirred solution of perchlorate **3** (2.0 g, 3.3 mmol) in dry methanol (100 mL), a solution of sodium methanolate in methanol (10 cg/g; 10 mL) was added and the mixture was shortly heated up. After cooling to room temperature, the dark solution was poured slowly with stirring into aqueous 2 mol·L$^{-1}$ NaOH (200 mL). The suspension formed was allowed to stand for ca. 12 h. Then, the dark-blue flocky precipitate was filtered off, washed thoroughly with water, and dried in vacuo. Twofold recrystallization with ethanol/water (3:2) yielded betaine **2** as dark-green glittering crystals (1.6 g; 94%) with m.p. 266–267 °C. – UV/Visible: $\lambda_{max}$/nm ($\varepsilon_{max}$) = 563 (3400) and 303 (44 300) in methanol; 836 (11 550), 520 (940), and 296 (30 000) in 1,4-dioxane. Visible absorption maxima of **2** for further 27 solvents of different polarity can be found in ref. [2a]. – $C_{37}H_{37}NO$ (511.7): calcd. 86.85, H 7.29, N 2.74; found C 87.09, H 7.23, N 2.81.

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