QUINONOID MESOIONS, (2,3-DIPHENYLTETRAZOL-5-YLIO)PHENOLATES

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Abstract: The synthesis and the properties of (2,3-diphenyltetrazol-5-ylio)phenolates are described as the first representatives of quinonoid mesoions.

Mesoionic compounds can be expressed by the general formula (1), where a - f are suitably substituted carbons or heteroatoms.<sup>1)</sup> When a benzene ring is inserted into the exocyclic e-f bond, a new type of mesoionic systems of the formula (2) is derived. This compound (2) can be regarded as a quinonoid analog of mesoions (1).<sup>2)</sup> In this paper, we describe the synthesis and the properties of (2,3-diphenyltetrazol-5-ylio)phenolates (3) as the first representatives of quinonoid mesoion (2).



Anisaldehydes (o-, m-, and p-) (4a - c) were converted to their phenylhydrazones (5a - c),<sup>3</sup>) which were coupled with benzenediazonium chloride to yield 1,5-diphenyl-3-(methoxyphenyl)formazanes (6a - c).<sup>4</sup>) The formazanes were oxidized with chromium trioxide<sup>5</sup>) or N-bromosuccinimide<sup>6</sup>) to 2,3diphenyl-5-(methoxyphenyl)tetrazolium salts (7a - c).<sup>7</sup>) Demethylation with boron tribromide gave 2,3-diphenyl-5-(hydroxyphenyl)tetrazolium bromides (8a - c). The phenolic tetrazolium salts (8a - c), the conjugate acids of quinonoid mesoions (3), are stable pale yellow crystals and the structures were fully characterized by their analytical<sup>7</sup>) and spectral data. The <sup>1</sup>H<sup>8</sup>) and <sup>13</sup>C NMR chemical shifts (Table 1) of the phenols (8a - c) are listed.

The compounds  $(\underline{8}a - c)$  are soluble in aq. alkali to form orange solutions of the mesoionic compounds  $(\underline{3}a - c)$ . The pK<sub>a</sub> values measured by a UV method are 7.75 ( $\underline{8}a$ ), 8.65 ( $\underline{8}b$ ), and 8.08 ( $\underline{8}c$ ), which are smaller by 1.3 -2.2 than that of phenol (pK<sub>a</sub> = 9.96), indicating that the acidity increases with the substitution of the electron-withdrawing tetrazolium ring. Isolation of  $\underline{3}a - c$  was achieved as follows. The phenolates ( $\underline{8}a - c$ ) were respectively dissolved in excess of an aqueous sodium hydroxide solution and the solvent was evaporated under vacuum, and the residues were chromatographed on

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Sephadex LH-20 using dichloromethane as an eluent to furnish purple crystals of hydrated quinonoid mesoions (3a - c). Compositions of the hydrates<sup>9)</sup> were determined by elemental analyses. They are stable on exposure to air at room temperature, though the m-isomer (3b) is somewhat less stable than the other isomers (3a) and (3c). Their melting points and <sup>1</sup>H NMR data are listed.<sup>9)</sup> The <sup>1</sup>H NMR spectra of 3a - c showed the signals of the phenolate ring protons at higher magnetic field than the corresponding protons of the conjugate acids ( $\underline{8}a$  - c). For example, the AA'BB' pattern of the *p*-isomer (8c) at  $\delta$  7.08 and 8.15 (*J*= 9 Hz) was shifted upfield to  $\delta$  6.29 and 7.74 (J= 9 Hz) by deprotonation. The chemical shifts of the oxygenbearing carbons of 3a - c were largely shifted (11.8 - 14.2 ppm) to lower magnetic field compared with those of  $\frac{8}{2}a$  - c (Table 1). This corresponds well to the chemical shift difference (12.7 ppm) between the corresponding carbons of phenol (155.6 ppm) and phenolate anion (168.3 ppm). On the other hand, the tetrazolium carbons and the carbons of the phenyl rings attached to the tetrazolium ring of 3a - c resonate at the almost coincident positions with those of  $\underline{8}a$  - c. These spectroscopic properties indicate that the compounds 3a - c can be regarded as phenolate anions substituted by a 2,3diphenyltetrazolium ring. The treatment of the solutions of 3a - c with tetrafluoroboric acid reversibly regenerates the conjugate acids ( $\frac{8}{2}a - c$ ) as the tetrafluoroborate salts in quantitative yield.

The electronic spectral data of 3a - c measured in acetonitrile are as follows;  $3a: \lambda_{max}$  220 nm (log  $\epsilon$  4.18), 258 (sh, 4.00), 381 (4.03), and 496 (2.59); 3b: 250 (4.42), 320 (sh, 3.64), and 535 (2.61); 3c: 213 (4.06), 228 (3.96), 300 (sh, 4.05), 347 (4.54), and 513 (2.68). The longest wavelength bands of 3a - c showed a large blue-shift on going from less polar to polar

Table 1. <sup>13</sup>C NMR of <u>8a</u> - c, <u>3a</u> - c, and <u>10</u> (DMSO-d<sub>6</sub>)

|            | C-1     | C-2                | C-3     | C-4                | C-5   | C-6                | c+    | Phenyl |       |       |       |
|------------|---------|--------------------|---------|--------------------|-------|--------------------|-------|--------|-------|-------|-------|
|            |         |                    |         |                    |       |                    |       | ipso   | ortho | meta  | para  |
| 8a         | 109.8   | 157.1              | 117.4   | 130.2 <sup>a</sup> | 120.1 | 134.6 <sup>a</sup> | 163.1 | 133.2  | 126.6 | 130.4 | 134.1 |
| ğь         | 124.0   | 117.9 <sup>b</sup> | 158.5   | 113.4 <sup>b</sup> | 131.4 | 120.6              | 164.1 | 133.0  | 126.5 | 130.2 | 134.0 |
| 8℃         | 113.5   | 129.4              | 117.0   | 162.2              | 117.0 | 129.4              | 164.5 | 133.1  | 126.5 | 130.4 | 134.0 |
| <u>3</u> a | 107.1   | 170.6              | 123.0   | 129.4 <sup>C</sup> | 108.6 | 133.2 <sup>C</sup> | 166.8 | 133.5  | 126.6 | 130.0 | 133.4 |
| Зр         | 124.0   | 123.0 <sup>d</sup> | 170.3   | 115.9 <sup>d</sup> | 130.3 | 107.5              | 166.4 | 133.1  | 126.4 | 130.2 | 133.8 |
| 3c         | 99.7    | 128.9              | 120.4   | 176.4              | 120.4 | 128.9              | 166.6 | 133.3  | 126.5 | 130.2 | 133.5 |
| 10         | 106.7   | 129.1              | 118.6   | 170.3              | 118.6 | 129.1              | 165.6 | 133.2  | 126.5 | 130.2 | 133.8 |
| a-d        | These v | alues ma           | ay be i | nterchar           | nged. |                    |       |        |       |       |       |

solvents; for example, the  $\lambda_{max}$  values of the lowest-excitation band of 3c are 528 nm (CH<sub>2</sub>Cl<sub>2</sub>), 524 (Me<sub>2</sub>C=O), 513 (MeCN), 467 (Pr<sup>i</sup>OH), 437 (EtOH), and 419 (MeOH). This indicates a large contribution of a polar canonical form (3) to the resonance hybrid for the ground state of the quinonoid mesoions (3a - c).<sup>10)</sup> In the IR spectra of 3a - c, intense absorptions appeared in the range of 1490 - 1436 cm<sup>-1</sup>. The mass spectra of the three mesoions (3a - c) are essentially same; the molecular ions were not observed but the characteristic fragment ion appeared at m/z 286, which is considered due to the mesoionic fulvalene (9)<sup>11</sup> arising from the elimination of CO from the mesoions (3a - c).

On addition of a slight excess of DBU to a suspension of &c in dichloromethane, &c went into solution and, within a few minutes, an orange solid was deposited, which was filtered and recrystallized from ethanol-ether to give orange crystals (10) [mp 179 °C (dec)]. This orange compound is not 3c but a



1 : 1 adduct (10) of 3c and 8c, based upon the elemental analysis and the electronic spectrum coinciding with the sum of the absorptions of both 3c and 8c with equal proportion. Moreover, the <sup>13</sup>C NMR chemical shifts of 10 are average of those of 3c and 8c (Table 1), indicating that 10 exists as the rapid equiliblium between 3c and 8c in a DMSO-d<sub>6</sub> solution. Similar adducts were also obtained from o- (8a) and m-isomers (8b) by the same method.

In summary, the first examples of quinonoid mesoions are synthesized and isolated as stable crystalline forms. Their spectroscopic properties clearly indicate that the mesoions are best expressed by a dipolar (tetrazoliumphenolate) structure. References and Notes

1) W. D. Ollis and C. A. Ramsden, Adv. Heterocycl. Chem., 19, 1 (1976); C. G. Newton and C. A. Ramsden, Tetrahedron, 38, 2965 (1982). 2) The quinonoid mesoion (2) is an isoelectronic compound with [6.7]quinaren-9-one which was recently fully characterized: K. Takahashi, T. Nozoe, K. Takase, and T. Kudo, Tetrahedron Lett., 25, 77 (1984). 3) P. Grammaticakis, Bull. Soc. Chim., 7, 527 (1940). 4) D. Jerchel and H. Fischer, Justus Liebigs Ann. Chem., 574, 85 (1951); V. N. Dubinina, L. V. Rodnenko, and G. N. Lipunova, Zh. Anal. Khim., 33, 1547 (1978). 5) J. N. Ashley, B. M. Davis, A. W. Nineham, and R. Slack, J. Chem. Soc., 1953, 3881. 6) W. Ried and D. Schendzielorz, Justus Liebigs Ann. Chem., 682, 156 (1965). 7) Satisfactory elemental analyses were obtained. 8) Melting points and <sup>1</sup>H NMR of  $\beta a - c$ : <sup>1</sup>H NMR (60 MHz, DMSO-d<sub>6</sub>)  $\delta/ppm$ 8a<sup>a</sup> 259 (dec) 7.00 - 8.10 (m, 14H, Ph and H-3 - H-6), 10.95 (s, 1H, OH) 8b258 (dec) 7.10 - 8.00 (m, 14H, Ph, H-2, and H-4 - H-6), 10.30 (s, 1H, OH) 7.08 (d, J=9 Hz, 2H, H-3 and H-5), 7.65 - 7.85 (m, 10H, Ph), 8c 280 (dec) 8.15 (d, J=9 Hz, 2H, H-2 and H-6), 11.00 (s, 1H, OH) <sup>a</sup>8a·EtOH (1:1 complex of 8a and EtOH). 9) Melting points and <sup>1</sup>H NMR of <u>3a</u> - c: θ<sub>m</sub>/°C <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>) δ/ppm 6.24 (t, J=8 Hz, 1H, H-5), 6.57 (d, J=8 Hz, 1H, H-3), 7.09 (t, J=8 Hz, 1H, H-4), 7.64 - 7.84 (m, 7H, H-6 and Ph), 7.91 (d, J=7 Hz, 4H, Ph) 3a.0.5H20 140 (dec) 6.64 (d, J=8 Hz, 1H, H-4), 7.01 (d, J=8 Hz, 1H, H-6), 3b.H.O 141 (dec) 7.17 (m, 2H, H-2 and H-5), 7.68 - 7.82 (m, 6H, Ph), 7.89 (d, J=7 Hz, 4H, Ph) 6.29 (d, J=9 Hz, 2H, H-3 and H-5), 7.63 - 7.81 (m, 6H, 3c · 2H\_0 154 (dec) Ph), 7.74 (d, J=9 Hz, 2H, H-2 and H-6), 7.87 (d, J=7 Hz, 4H, Ph) 10) N. S. Bayliss and E. G. McRae, J. Phys. Chem., 58, 1002 (1954); E. M. Kosower, J. Am. Chem. Soc., 80, 3253 (1958). 11) 1,3-Diphenyltetrazol-5-yliocyclopentadienide, an isomeric compound of 9, was recently synthesized: S. Araki and Y. Butsugan, J. Chem. Soc., Chem.

Commun., 1983, 789; Tetrahedron Lett., 25, 441 (1984); J. Chem. Soc., Perkin Trans. 1, 1984, 2545.

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