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# 3,4-Dibromo-2,5-bis-dicyanomethylene-1-(1-pyridinio)-3-cyclopentene-1-ides: Novel Pyridinium Ylides of the Cylopentadiene Series¶

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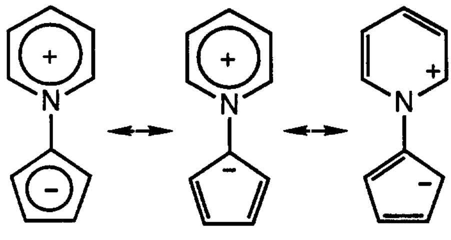
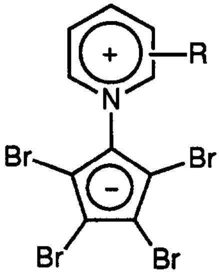
**Abstract:** Pyridiniotetrabromocyclopentadienides react with tetracyanoethylene to form the title ylides in which the pyridinium ring and the cyclopentenide moiety are orthogonally arranged.

Pyridiniocyclopentadienides **1** can be viewed as ylides **1'** with a cyclopentadiene moiety or as 1,4-dipoles **1"**. Due to the instability of **1** little is known about its chemistry. Reactions with tetracyanoethylene (TCNE) have been mentioned.[1] The 1,4-dipolar character of **1** shows up in its reactions with acetylenedicarboxylates.[2] Pyridiniotetrabromocyclopentadienides are more stable than **1**. **2a**[3] has been prepared in low yield by reacting a solution of ferrocene in pyridine with bromine (dissolved in $CCl_4$) followed by chromatography.[4] We found that the low yield is due to an autocatalytic decomposition of **1b** during chromatography. The yield can be substantially increased by dissolving the oily reaction product in ethyl acetate or cyclohexane, extracting the solution with water and rapid chromatography of the dried ($Na_2SO_4$) organic phase using a very short column



**1** **1'** **1"**

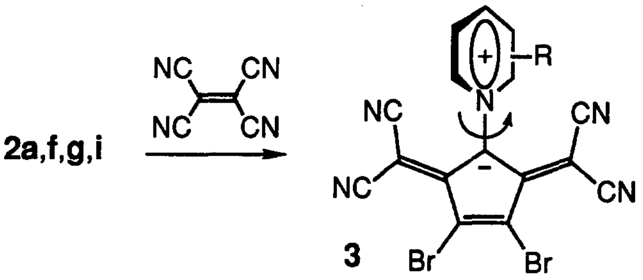


**2**

**2a**: R = H
**2b**: R = 4-Me
**2c**: R = 3-Me
**2d**: R = 2-Me
**2e**: R = 4-OMe
**2f**: R = 4-$CO_2$Me
**2g**: R = 3-$CO_2$Me
**2h**: R = 4-CN
**2i**: R = 4-$NMe_2$

(10 cm, silica gel). In this way we have synthetized a number of pyridiniotetrabromocyclopentadienides **2** (**2b**: yield 11%, orange needles, dec. 154 °C; **2c**: 29%, orange needles, dec. 120 °C; **2d**: 27%, orange needles, dec. 153 °C; **2e**: 45%, pale yellow needles, dec. 103 °C; **2f**: 35%, deep blue needles, dec. 135 °C; **2g**: 12%, wine red needles, dec. 144 °C; **2h**: 5%, black-blue crystals, dec. 153 °C; **2i**: [ferrocene and DMAP were dissolved in $CH_2Cl_2$ and a solution of bromine in $CCl_4$ added at 0 °C; the precipitate was collected by filtration and washed with $CHCl_3$] 3%, pale green needles, m.p. 287 °C).

When **2a,f,g,i** are reacted with TCNE in tetrahydrofuran or even better dimethylformamide at room temperature, the novel ylides **3** are formed in fair yields (**3a**: yield 43%; black-violet needles, dec. > 280 °C; $^1$H NMR ([D$_7$]DMF): $\delta$ = 8.47 (m; 2 H, β-H), 8.97 (m; 1 H, γ-H), 9.37 (m; 2 H, α-H); IR (KBr): $\tilde{\nu}$ = 2200 cm$^{-1}$, 2185 (C≡N), 1625 (C=N); UV-vis: $\lambda_{max}$ (lg $\varepsilon$) = DMSO: 390 nm (sh), 407 (4.33), 427 (sh), 630 (4.07), 665 (4.04), 728 (3.72, sh)/ MeCN: 218 (4.39), 236 (4.39), 258 (4.23, sh), 385 (sh), 399 (4.38), 419 (sh), 615 (4.07), 640 (4.07), 702 (3.76, sh)/ $CH_2Cl_2$: 237, 255 (sh), 385 (sh), 403, 423, 605, 635, 692 (sh); **3f**: 46%; violet powder, dec. >200 °C; **3g**: 50%; violet needles, dec. > 200 °C; **3i**: 62%; deep violet needles, dec. > 280 °C, UV-vis (MeCN): $\lambda_{max}$ = 630 nm, 670 (sh), 730 (sh)). The rate of the reaction follows the order **2a** > **2g** > **2f** which is in accord with the negative charge densities in the 5-membered rings of **2**.



**3a** shows positive solvatochromism in contrast to **1**[5] (charge transfer from the cyclopentadienide to the pyridinium ring).[6] Obviously, there is no charge transfer in **3** from the anionic moiety to the pyridinium ring. A PPP-SCF calculation leads to the conclusion that the long-wavelength absorption of **3** originates essentially from the anionic moiety of **3**. The solvatochromism is a consequence of the different charge densities in the frontier orbitals (charge transfer from the HOMO to the LUMO; cf. Figure 1). Based on the PPP-SCF calculation the longest-wavelength absorption of the anionic

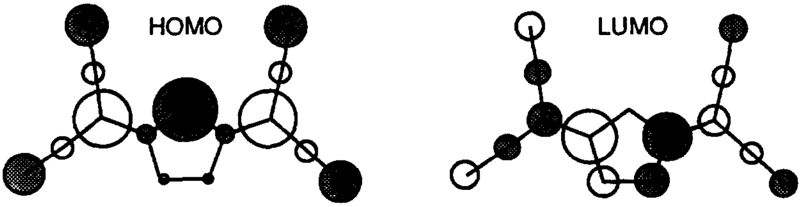
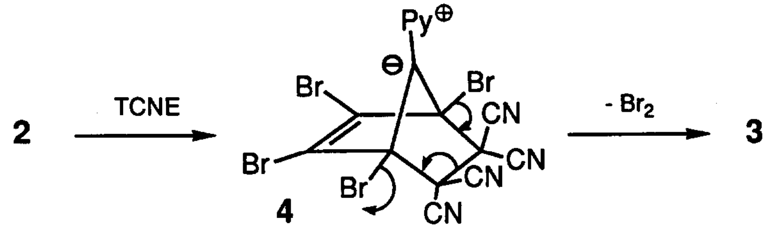


Fig. 1. Charge distribution in the frontier orbitals of the anionic moiety of **3**

moiety of **3** is estimated to occur at 1000 nm; the pyridinium ring in **3** as an electron-withdrawing group is expected to cause a hypsochromic shift.

The formation of **3** from **2** and TCNE can be rationalized by assuming the formation of the Diels-Alder adduct **4** in the first step, followed by 1,4-elimination of bromine which is then trapped by **2** (in the reaction with **2f** a by-product **2f** × $Br_2$ could be isolated). A similar reaction has been observed between 5,10-dihydro-5,10-dimethylphenazine and TCNE.[7]



Single crystals of **3a** were grown by slow diffusion of chloroform into a saturated solution in dimethylformamide over 6 weeks. The X-ray crystallographic analysis[8] (Figures 2 - 4) reveals the nearly orthogonal arrangement of the two rings (twist angle 85.1°) which makes a resonance interaction between the two rings highly improbable. As concluded from the positive solvatochromism the same situation prevails in solution. The length of the C1-N5 bond (145 pm) corresponds to that of a normal C-N single -bond (147 pm)[9]. **3a** crystallizes centrosymmetrically, the head-to-tail arrangement of the dipolar molecules beeing reversed in the adjacent layers.

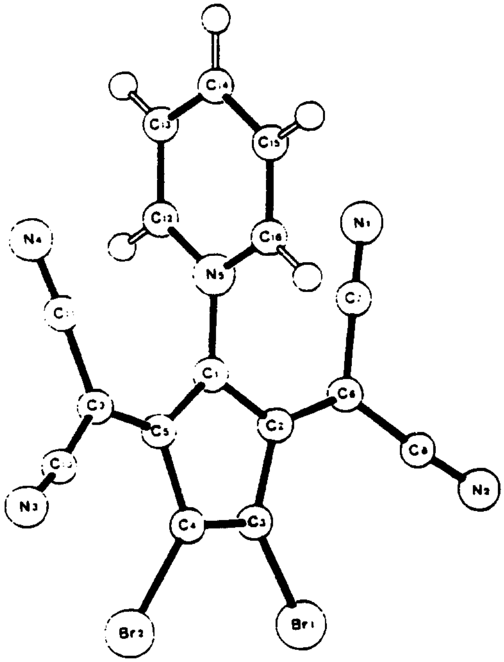


Fig. 2. ORTEP view of the molecular structure of **3a**, showing the atom labeling scheme, selected bond lengths (Å) and angles (°): C1-N5 144.6, C1-C2 140.4, C2-C3 147.8, C3-C4 135.0, C2-C6 138.8, C6-C7 144.4, C7-N1 113.9, C12-N5 135.2, C12-C13 136.6, C13-C14 137.4; C2-C1-N5 123.8, C2-C1-C5 111.5, C1-C2-C6 129.5, C2-C3-C4 109.3.

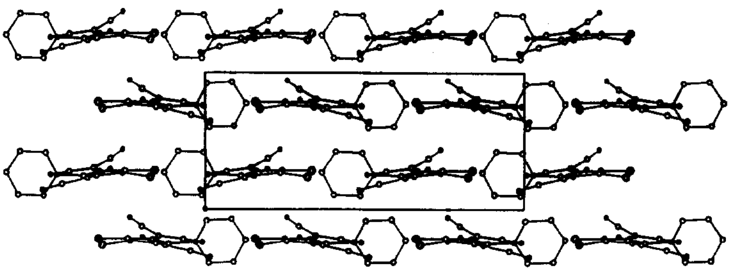


Fig. 3. Crystal structure of **3a**, a/b projection

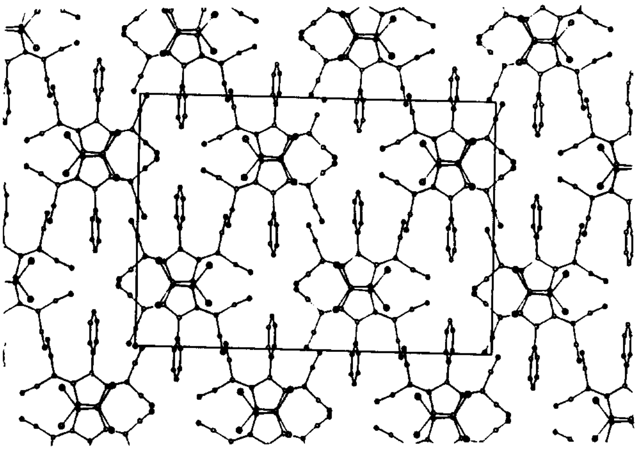


Fig. 4. Crystal structure of **3a**, b/c projection

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## References and Notes

¶ Dedicated to Professor Wolfgang Steglich on the occassion of his 60th birthday.

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8. X-ray Crystallographic Analysis of **3a**: Syntex $P2_1$ diffractometer, Cu-$K_\alpha$ radiation,T = 296 K. Crystallographic data: $C_{16}H_5Br_2N_5$, M = 427.07, orthorhombic, 0.45 × 0.13 × 0.10 mm, space group Pbca, $a$ = 24.230(3) Å, $b$ = 17.037(3) Å, $c$ = 7.3050 (10) Å, V = 3015.6(7) Å$^3$, Z = 8, $D_{calcd}$ = 1.881 g cm$^{-3}$, μ(Cu-$K_\alpha$) = 68.73 cm$^{-1}$. ω–scan 3.67° < Θ < 46.4°. 1972 reflections collected, 1972 independent reflections, and 1972 "observed" with $I > 2\sigma(I)$. Refinement full-matrix least squares on $F^2$ gave residuals R and $R_W$ of 0.0318 and 0.0887, respectively; largest residual densities = 0.54/ -0.53 e/Å$^3$. Supplementary material on the X-ray structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-57606, the names of the authors and the journal citation.
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