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Tetrabenzo[*a*,*c*,*h*,*j*]phenoxazine-18-yl a new stable neutral radical

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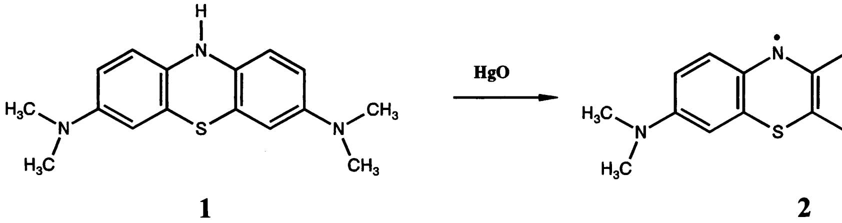
Abstract—The known 18*H*-tetrabenzo[*a*,*c*,*h*,*j*]phenoxazine (**3**) forms a highly stable planar aromatic neutral radical **4**. The radical forms with iodine a new triiodide, that shows a strong EPR signal too. © 2001 Elsevier Science Ltd. All rights reserved.



Scheme 1.

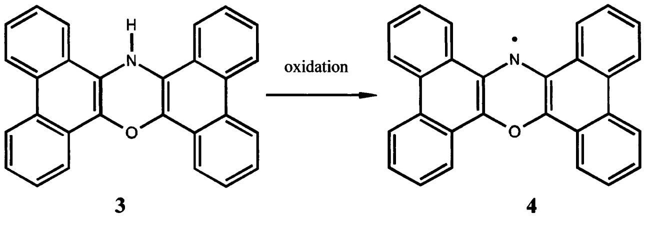
In recent years organic radicals have been intensively investigated. For example free nitroxyl radicals have been used in kinetic studies of complexation reactions.[1] Organic radicals were also investigated in connection with molecular based magnetism[2,3] and electric conductivity[4] to design new magnetic materials, molecular conductors and superconductors. So far there are not many stable neutral organic radicals known which are planar and have an aromatic structure. As we found earlier, some nitrogen containing heterocycles like the phenothiazine derivative leucomethylene blue **1** are easily oxidized by HgO to the free neutral radical **2** (Scheme 1).[5]

However, this radical is not very stable, due to the easy oxidation to its cationic form. In connection with our studies towards new organic materials, we found that the 18*H*-tetrabenzo[*a*,*c*,*h*,*j*]phenoxazine (**3**) which is known since 1895[6] forms a highly stable neutral radical **4** (Scheme 2).

Radical **4** (M^+ 382) has a very strong EPR signal (Fig. 1) that shows no loss of activity after 5 months.

We prepared **3** according to the procedure of Bamberger and Grob[7] from phenanthrenequinone and phenylhydrazine. The crude product is an ocher colored amorphous powder. The weak EPR signal (Fig. 2) seems to be caused by partial oxidation of **3** with air. The IR spectrum shows a weak NH absorption band at 3320 cm^{-1}.

Crystallisation from naphthalene (0.4 g/40 g) yields fine dark colored needles with a green metallic luster, after the naphthalene was removed by diethyl ether. The product has a very high melting point (350°C) and is almost insoluble in the most common organic solvents. The crystals show a strong EPR signal (Fig. 1). As we found there is no need to add an oxidant like HgO but it helps to bubble air to the hot naphthalene solution. If iodine is added in excess to the naphthalene solution,



Scheme 2.

Keywords: tetrabenzo[*a*,*c*,*h*,*j*]phenoxazine-18-yl; tetrabenzo[*a*,*c*,*h*,*j*]-phenoxazine-18-yl-triiodide; radical.

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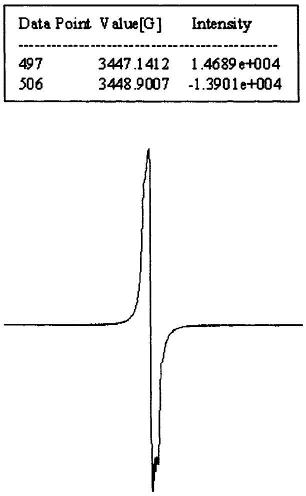

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Data Point  Value[G]     Intensity
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506         3448.9007   -1.3901e+004
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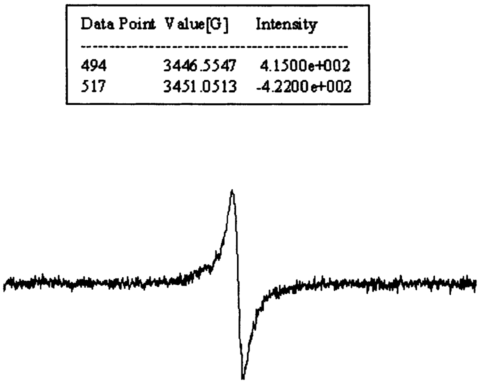
Figure 1. EPR spectrum of **4**.



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517         3451.0513   -4.2200e+002
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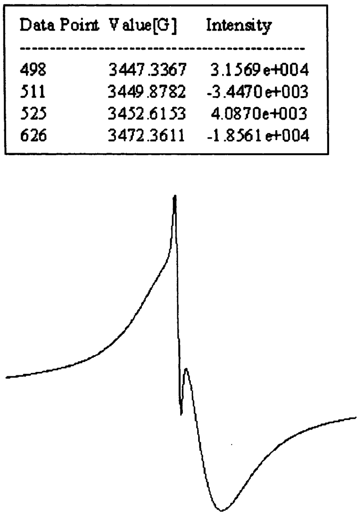
Figure 2. EPR spectrum of crude **3**/**4**.



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Data Point  Value[G]     Intensity
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498         3447.3367    3.1569e+004
511         3449.8782   -3.4470e+003
525         3452.6153    4.0870e+003
626         3472.3611   -1.8561e+004
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Figure 3. EPR signal of the triiodide derivative of **4**.

the isolated crystals have a bronze metallic luster. This compound shows an EPR signal with high relative intensity too (Fig. 3) which disappears almost totally after five months (Fig. 4). According to its elemental analysis we presume that this is a new unknown triiodide derivative of the radical **4** (mp 310°C, decomp.).

The new radicals are highly interesting substances. The X-ray structures and the physical and chemical properties are under investigation. We also intend to synthesize the Se, S and As derivatives of **3** expecting new radicals with interesting magnetic and electric properties.

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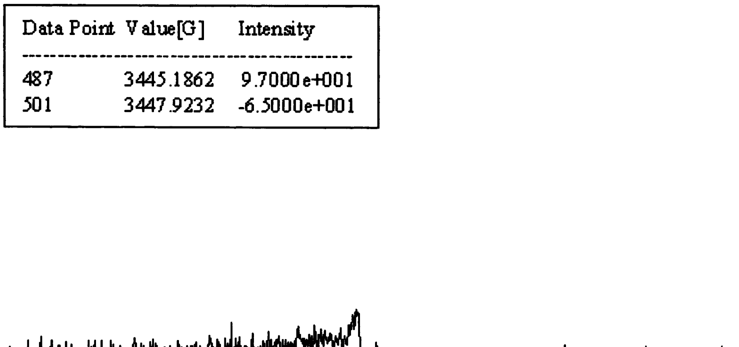

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Data Point  Value[G]     Intensity
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487         3445.1862    9.7000e+001
501         3447.9232   -6.5000e+001
```

Figure 4. EPR signal of the triiodide derivative of **4** after 5 months.

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