

# Synthesis and Characterization of a Novel Conformation of 2,9,10-Tribromoanthracene-1,4-dione

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**Abstract** Synthesis and X-ray analysis of single crystals of 2,9,10-tribromoanthracene-1,4-dione **4** has been described and its novel conformation is reported. Single crystals were grown by slow evaporation technique from toluene solution at  $-15\text{ }^{\circ}\text{C}$ . The compounds have been characterized by elemental analysis, FT-IR, Mass and NMR spectroscopy. The compound crystallizes in the triclinic space group  $P\bar{1}$  with unit cell dimensions  $a = 7.6842(2)$ ,  $b = 9.4865(2)$ ,  $c = 19.9388(4)\text{ \AA}$ ,  $\alpha = 78.784(5)$ ,  $\beta = 76.980(5)$ ,  $\gamma = 67.834(4)\text{ \AA}$ ;  $V: 1,301.75(7)\text{ \AA}^3$ ;  $Z = 2$ ,  $R_1 = 0.0748$ , and  $wR_2 = 0.131$ .

**Keywords** 1,4-Anthraquinone · Bromoanthraquinone · Single crystals · X-ray diffraction

## Introduction

Natural and synthetic anthraquinones have received a great deal of attention due to their wide application such as dyes,

biologically active substances, medical agents, analytical reagents, indicators, catalysts for industrially important processes and data storage materials [1]. Although 9,10-anthraquinones have been extensively studied, 1,4-anthraquinones have been scarcely studied [2]. There are many 1,4-anthraquinones used as tumor-cell-growth inhibitors [3, 4], optoelectronic dyes [5] and organic conductors [6]. Also this type of anthraquinones such as adriamycin and daunomycin are considered to be the basic building for the broad-spectrum anti-cancer drugs. For these reason, interest in bioactive 1,4-anthraquinones has increased considerably [7].

Most recently [8], we have developed a selective and efficient method for the preparation of 2,9,10-tribromoanthracene-1,4-dione (**3**) from 2,9,10-tribromo-1,4-dihydroanthracene-1,4-diol (**2**). The reaction of (1R,2S,3R,4S)-2,3,9,10-tetrabromo-1,2,3,4-tetrahydroanthracene-1,4-diol (**1**) with sodium methoxide afforded tribromodihydroxyanthracene-1,4-diol **2** and whose oxidation with PCC gave 2,9,10-tribromoanthracene-1,4-dione (**3**) (Scheme 1).

However, when we reacted compound **1** with PCC we encountered a novel conformer of **3** (Scheme 2). In this study, we report reaction procedure and detailed comparative spectral analysis of the both compounds **3** and **4**. We also report here its crystal structure analysis obtained from single crystal X-ray diffraction method.

## Experimental Procedure

### Physical Techniques and Materials

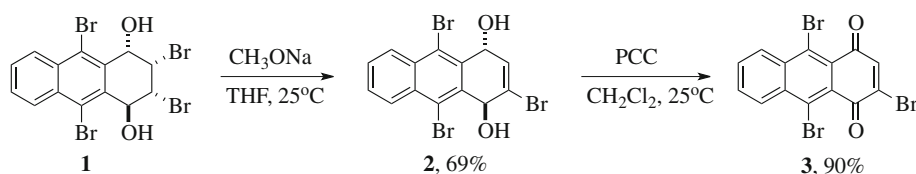
Dihydroxyanthracene **1** was prepared by silver ion assisted hydrolysis of (1R,2S,3R,4S)-1,2,3,4,9,10-hexabromo-1,2,3,4-tetrahydroanthracene (**6**) [8]. Other reagents and solvents for synthesis, growth and analysis were commercially

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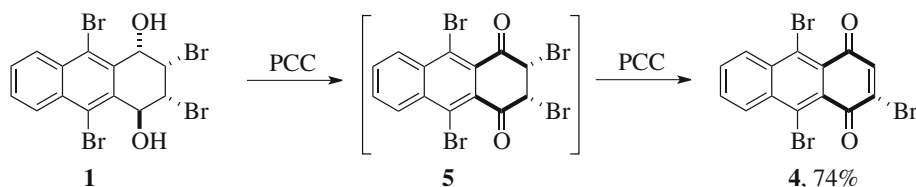
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**Scheme 1** Synthesis of 2,9,10-tribromoanthracene-1,4-dione (**3**)



**Scheme 2** Synthesis of tribromoanthracene-1,4-dione (**4**)



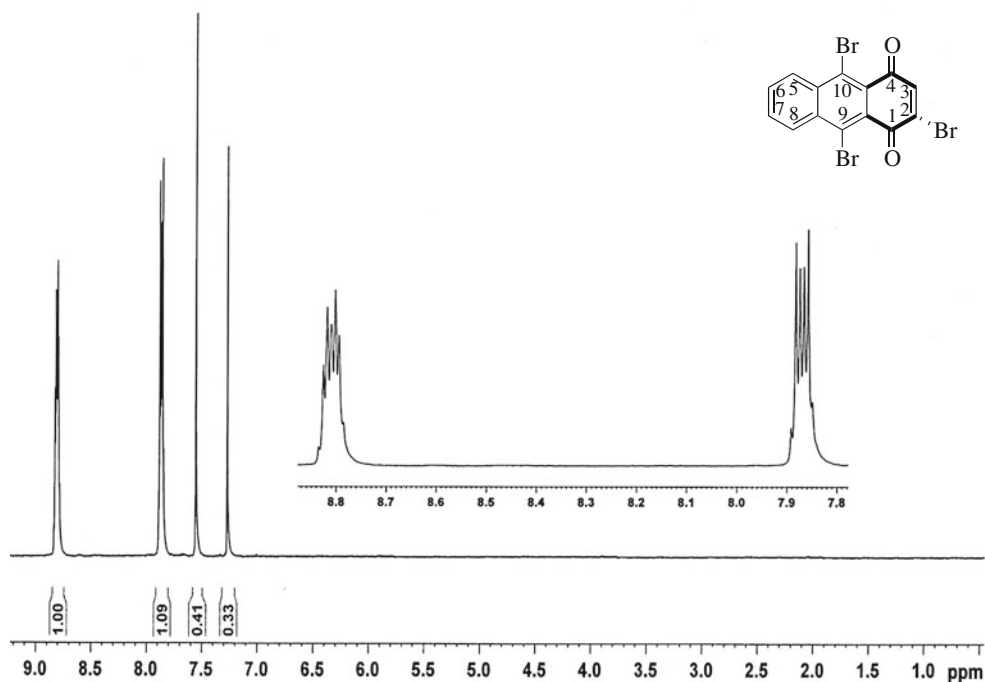
available. Thin layer chromatography was carried out on Merck 0.255 mm silica gel F254 analytical aluminum plates and spots were visualized with UV fluorescence at 254 nm. Melting point was determined on a Thomas-Hoover capillary melting point apparatus. Elemental analysis was carried out using a LECO-CHNS-932 analyzer. NMR spectra were measured with BRUKER AVANCE II spectrometer at 400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$  NMR. IR spectrum was recorded on a JASCO FT-IR 430 spectrophotometer as a KBr pellet. Mass spectrum was recorded on a THERMO FINNIGAN spectrometer.

#### Preparation and Crystal Growth of 2,9,10-Tribromo-1,4-anthraquinone **4**

To a solution of pyridinium chlorochromate (PCC) (448 mg, 2.08 mmol) in methylene chloride (35 mL) was added a solution of dihydroxyanthracene **1** (500 mg, 0.94 mmol) in methylene chloride (12 mL). The mixture was stirred at ambient temperature for 3 days. Reaction progress was monitored by TLC for consumption of the starting material (TLC monitoring). After the residue was filtered through a short silica gel (10 g) column eluting with methylene chloride (120 mL), 2,9,10-tribromoanthracene-1,4-dione (**4**) was recrystallized from toluene yield 335 mg (80 %). Yellow crystals. Anal. Calc. for  $\text{C}_{14}\text{H}_5\text{Br}_3\text{O}_2$ : C, 37.79; H, 1.13, Found: C, 37.73; H, 1.29 IR (KBr pellet,  $\text{cm}^{-1}$ ): 3442, 3060, 2921, 2846, 1673, 1654, 1621, 1604, 1471, 1375, 1319, 1247, 1234, 1164, 1149, 1124, 1020, 914, 889, 838, 755, 701, 566, 514, 466, 431, 410, 401;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.79–8.84 (m, 2H,  $\text{H}_5$  and  $\text{H}_8$ ), 7.85–7.89 (m, 2H,  $\text{H}_6$  and  $\text{H}_7$ ), 7.56 (s, 1H,  $\text{H}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  180.7, 177.4, 141.0, 139.1, 135.2, 135.0, 131.61, 131.60, 131.0, 130.8, 128.0, 127.9, 127.5, 126.7. MS (APCI)  $m/z$  489.0 ( $\text{M}^+ + \text{Na} + \text{NH}_4 + 3\text{H}$ ), 467.9 ( $\text{M}^+ + \text{Na}$ ), 445.0 ( $\text{M}^+$ ), 421.1, 395.0, 366.1, 355.0, 346.1, 329.0, 306.0, 297.0, 283.0, 255.1, 240.1, 228.1 ( $\text{M}^+ - 3\text{Br} + \text{Na} + 2\text{H}$ ), 212.1, 205.1, 156.9, 149.1, 136.0.

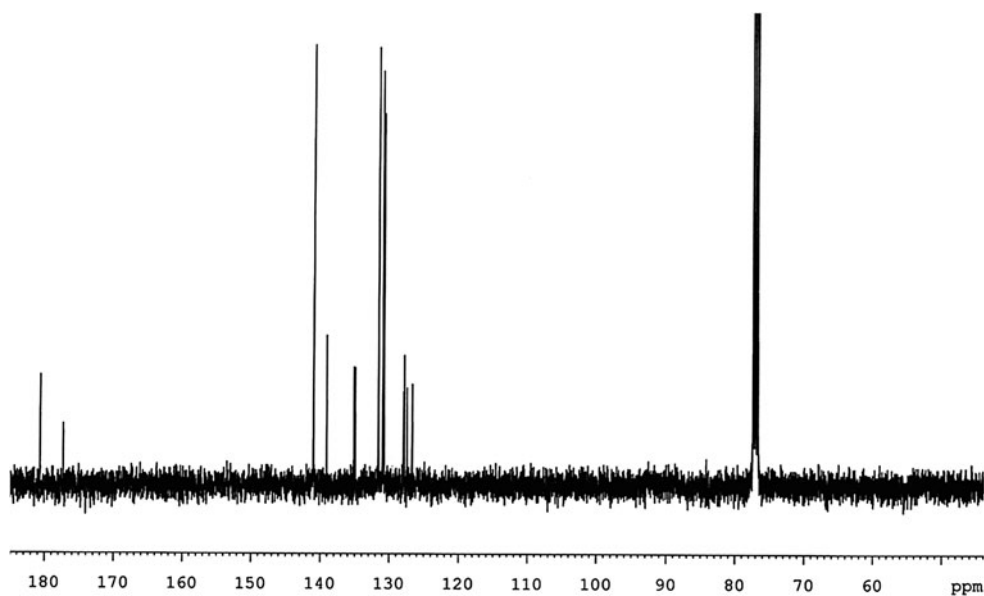
**Table 1** Spectral data, elemental analysis, melting points,  $R_f$  values and colours of the both compounds **3** and **4**

Compound		
MS (APCI) $m/z$	489.1 ( $\text{M}^+ + \text{Na} + \text{NH}_4 + 3\text{H}$ ) 467.9 ( $\text{M}^+ + \text{Na}$ ) 446.0 ( $\text{M}^+ + \text{H}$ ) 421.1, 409.0 ( $\text{M}^+ - \text{Br} + \text{NH}_4 + \text{Na} + 3\text{H}$ ) 386.1 ( $\text{M}^+ - \text{Br} + \text{NH}_4 + 3\text{H}$ ) 355.0, 329.0 310.2 ( $\text{M}^+ - 2\text{Br} + \text{Na} + 2\text{H}$ ) 271.0, 254.0 227.1 ( $\text{M}^+ - 3\text{Br} + \text{Na} + \text{H}$ ), 149.1	489.0 ( $\text{M}^+ + \text{Na} + \text{NH}_4 + 3\text{H}$ ) 467.9 ( $\text{M}^+ + \text{Na}$ ), 445.0 ( $\text{M}^+$ ) 421.1, 395.0, 366.1 355.0, 346.1, 329.0 306.0, 297.0, 283.0 255.1, 240.1 228.1 ( $\text{M}^+ - 3\text{Br} + \text{Na} + 2\text{H}$ ) 212.1, 205.1, 156.9 149.1, 136.0
$^1\text{H}$ NMR ( $\delta$ )	8.81 (s, 1H, $\text{H}_3$ ) 8.74 (m, 1H, $\text{H}_8$ ) 8.48 (m, 1H, $\text{H}_5$ ) 7.84 (m, 2H, $\text{H}_6$ and $\text{H}_7$ )	7.56 (s, 1H, $\text{H}_3$ ) 8.79–8.84 (m, 2H, $\text{H}_5$ and $\text{H}_8$ ) 7.85–7.89 (m, 2H, $\text{H}_6$ and $\text{H}_7$ )
$^{13}\text{C}$ NMR ( $\delta$ )	177.0, 174.3, 146.1, 134.7, 134.1, 132.5, 131.8, 131.6, 131.2, 130.3, 130.0, 129.7, 128.1, 124.3	180.7, 177.4, 141.0, 139.1, 135.2, 135.0, 131.61, 131.60, 131.0, 130.8, 128.0, 127.9, 127.5, 126.7
Elemental analysis $\text{C}_{14}\text{H}_5\text{Br}_3\text{O}_2$ (444.9)	Found: C, 37.79; H, 1.31 Anal. calc.: C, 37.79; H, 1.13	Found: C, 37.73; H, 1.29
Melting point	251.5–252.5 °C	172–173 °C
$R_f$ (1:9 ethylacetate/hexane)	0.17	0.40
Colour	Red	Yellow



**Fig. 1**  $^1\text{H}$  NMR spectrum of the compound **4** (400 MHz,  $\text{CDCl}_3$ )

**Fig. 2**  $^{13}\text{C}$  NMR spectrum of the compound **4** (100 MHz,  $\text{CDCl}_3$ )



## Characterization

### Synthesis and Characterization

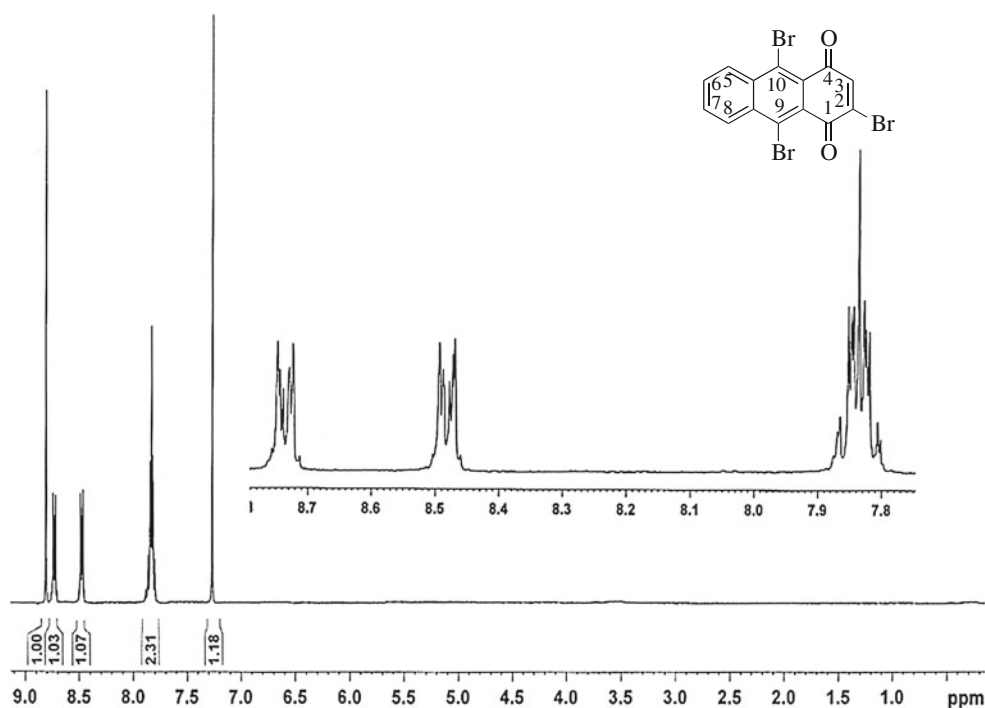
The PCC oxidation of dihydroxyanthracene **1** in dichloromethane at room temperature yielded the bromoanthraquinone **4** as a sole product in a yield of 80 % (Scheme 2).

Correct elemental and mass spectral analysis of compound **4** confirmed formula  $\text{C}_{14}\text{H}_5\text{Br}_3\text{O}_2$ . The compound

gives a mass spectrum with peaks at  $m/z$  at 489.0 ( $\text{M}^+ + \text{Na} + \text{NH}_4 + 3\text{H}$ ) and 445.0 ( $\text{M}^+$ ).

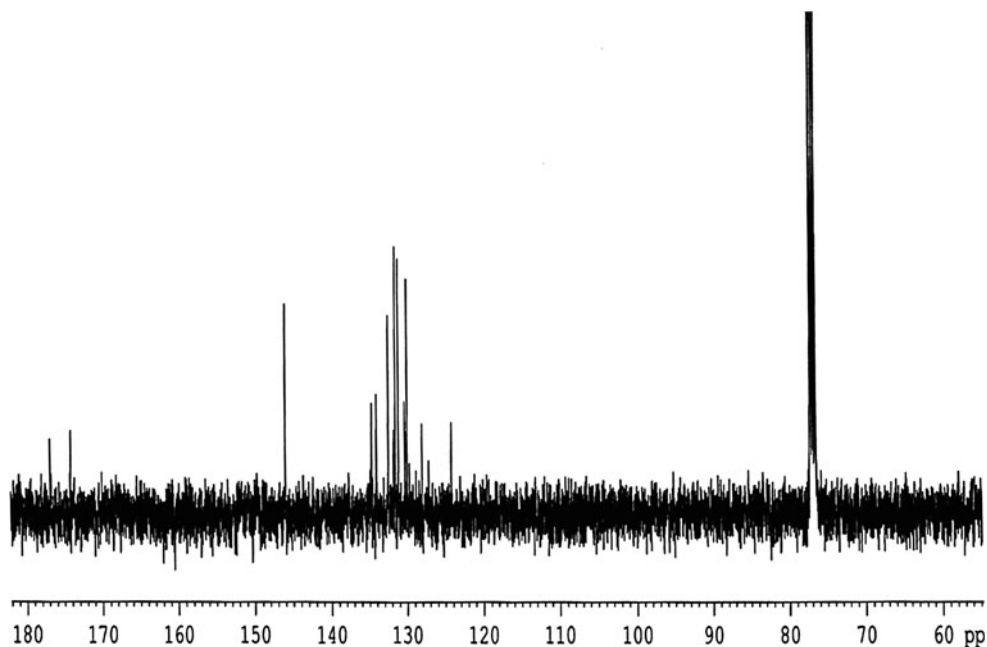
Although elemental and mass spectral analysis indicate same values for tribromides **3** and **4**. However, both compound's NMR spectra (Figs. 1, 2, 3, 4), melting points and colors are quite different from each others (Table 1).

$^1\text{H}$  NMR spectrum of compound **4** consists of three signal systems; two aryl multiplets at  $\delta$  8.79–8.84 for  $\text{H}_5$  and  $\text{H}_8$  and at  $\delta$  7.85–7.89 for  $\text{H}_6$  and  $\text{H}_7$ , and an olefinic



**Fig. 3**  $^1\text{H}$  NMR spectrum of 2,9,10-tribromoanthracene-1,4-dione **3** (400 MHz,  $\text{CDCl}_3$ )

**Fig. 4**  $^{13}\text{C}$  NMR spectrum of the compound **3** (100 MHz,  $\text{CDCl}_3$ )



singlet at  $\delta$  7.5 (Fig. 1).  $^{13}\text{C}$  NMR spectrum, consisting of 14 signals, confirms the structure with two carbonyl signals at 180.7 and 177.4 ppm respectively and no aliphatic signals (Fig. 2).

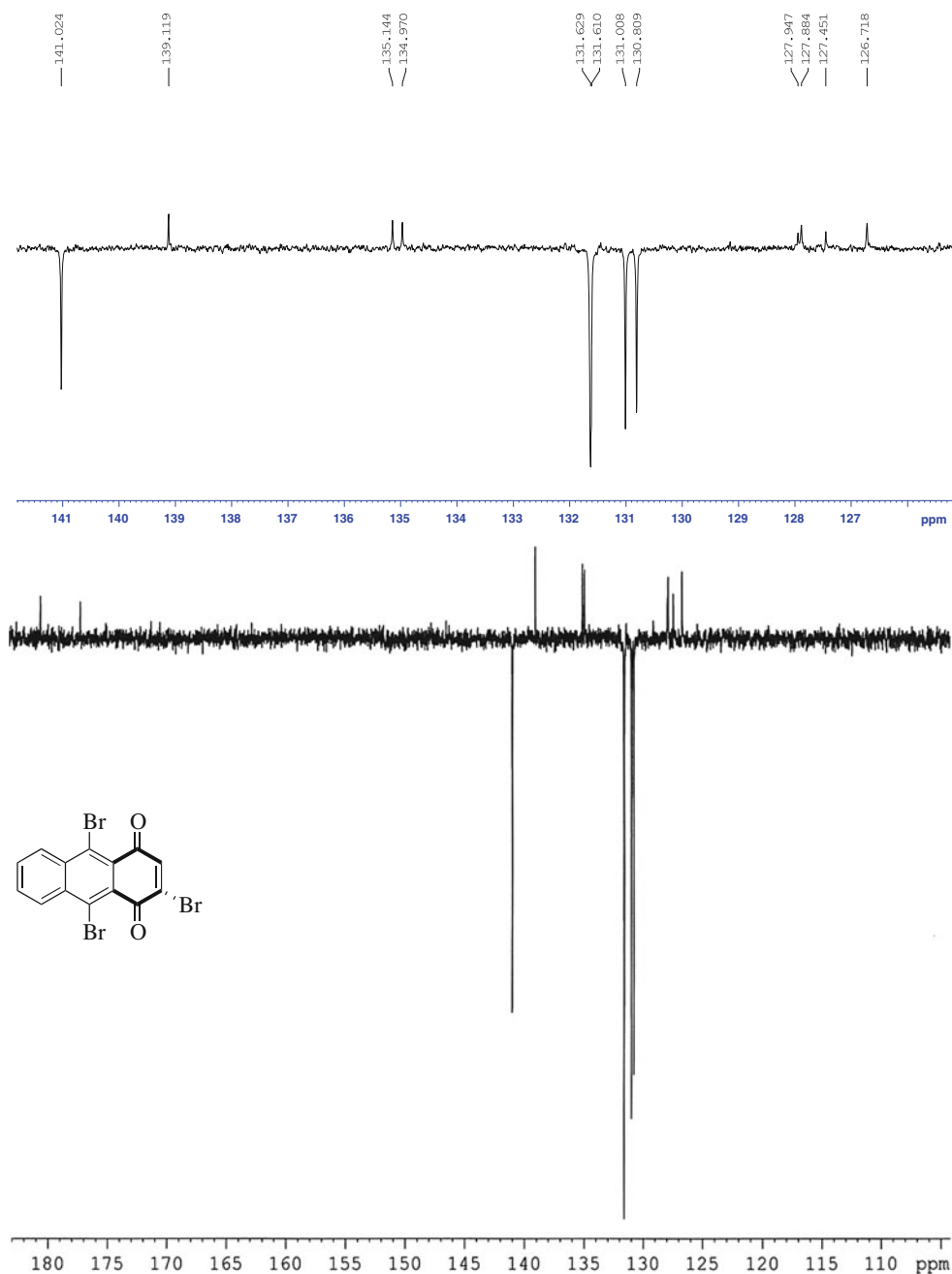
We also investigated APT and HMBC spectra of the both compounds.

APT spectra for the compounds **4** and **3** indicate existence of two carbonyl, five CH and seven C groups

(Figs. 5, 6). In the HMBC spectra of the both compounds, H3 proton for two compounds is located same positions as assigned correlation of carbonyl groups and H3 protons (Figs. 7, 8).

The all spectral data point same compound. Therefore, it is difficult to distinguish two compounds by NMR methods. Finally, we decide to make X-ray analysis of the compound **4**. For preparing suitable crystals for **3** and **4**,

**Fig. 5** The APT spectrum of compound **4** (100 MHz, DMSO- $d_6$ )



many attempts were made. We only obtained suitable crystals for compound **4**.

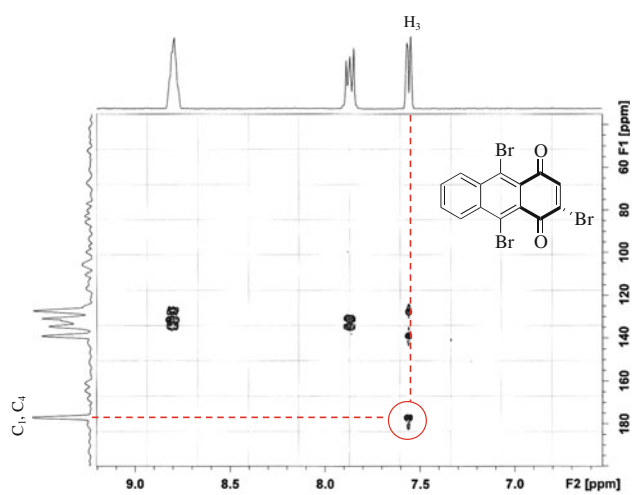
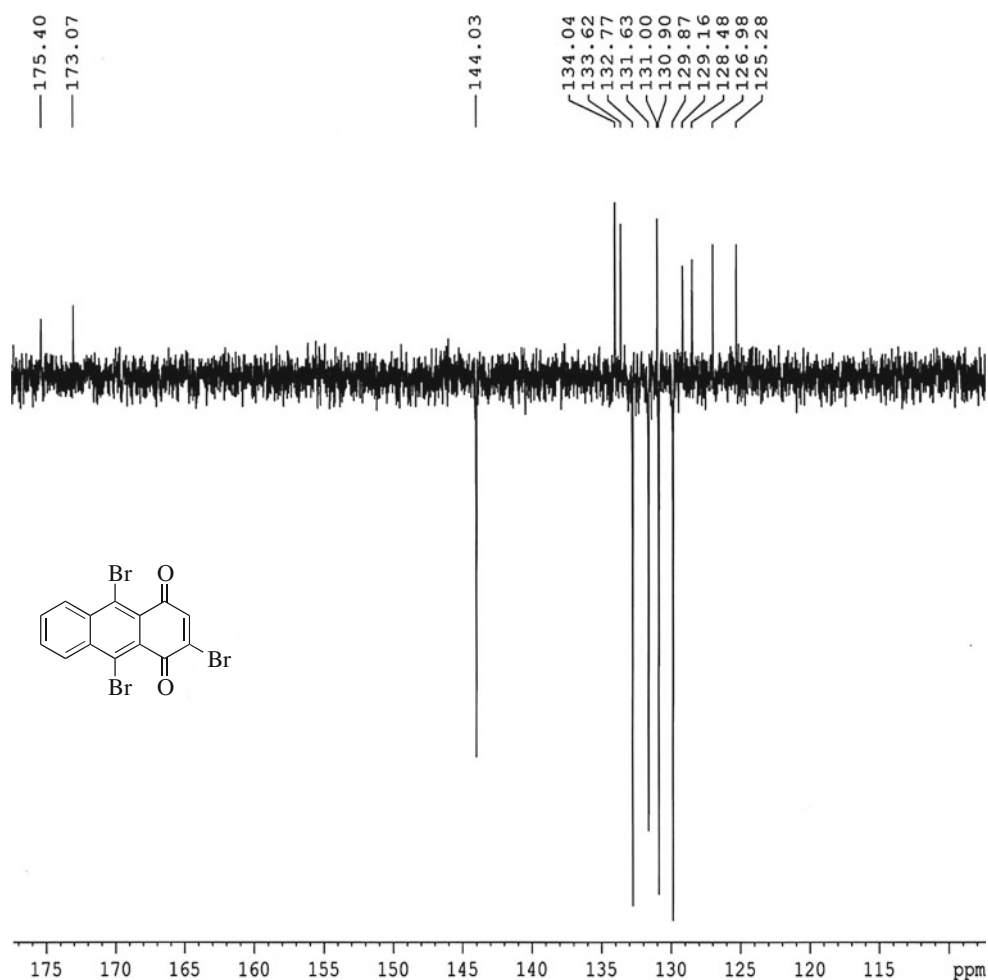
The X-ray analysis clearly shows the exact configuration of **4**, which is a conformer of compound **3**. We assume that the compound **3** is in planar structure and the increased conjugation is responsible for its dark red color. The bond bending at the quinone ring explains why compound **4** is light yellow (Fig. 9).

It is expected that the bending in compound **4** (Fig. 9) led to a decrease in the  $\gamma$ -Gauche effect between the bromine atoms and the carbonyl groups. Indeed, when compared the

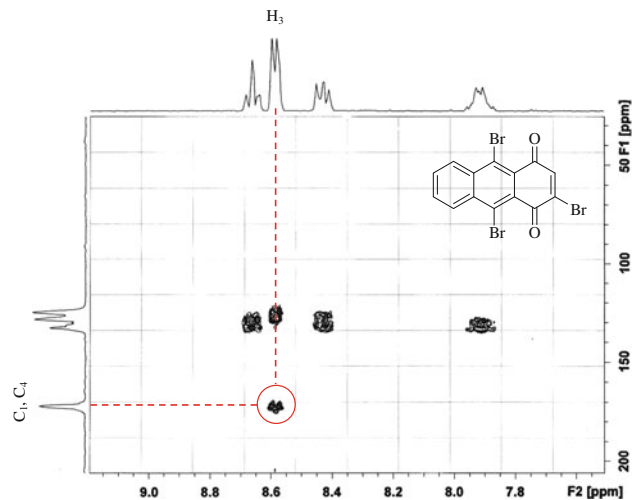
$^{13}\text{C}$  NMR values of the resonance of C9 and C10 at both compounds, those of compound **4** shift downfield 3 Hz (177.0  $\rightarrow$  180.7) and 4 Hz (174.3  $\rightarrow$  177.4). It can be attributed to decreased planarity of the quinone ring in compound **4**.

There are two molecules in the asymmetric unit of the compound **4**, one is a conformational isomer of the other, and all bond distances have normal values. The conformer **A** is almost planar (Fig. 10b), maximum deviation from the mean plane of the C8/C13 cyclohexene fragment is  $-0.013 \text{ \AA}$  for atom C13, there is a weak conjugation between these

**Fig. 6** The APT spectrum of compound **3** (100 MHz, DMSO- $d_6$ )



**Fig. 7** The HMBC spectrum of compound **4** (400 MHz DMSO- $d_6$ )

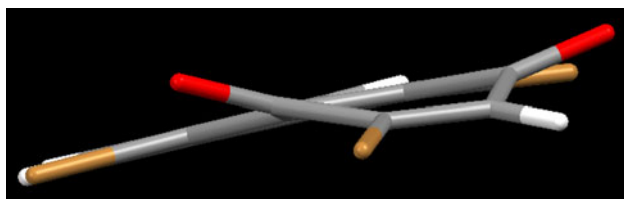


**Fig. 8** HMBC spectrum of 2,9,10-tribromoanthracene-1,4-dione **3** (400 MHz, DMSO- $d_6$ )

fragments of the molecule. In conformer **B**, ketone groups are twisted out due to steric hindrances. The C24–Br6 bond length is 1.858 (3) Å. As can be seen from crystal structure, Br3 and Br6 were surrounded by different atom symmetry.

### Crystallography

For the crystal structure determination, single-crystal of compound **4** was used for data collection on a four-circle

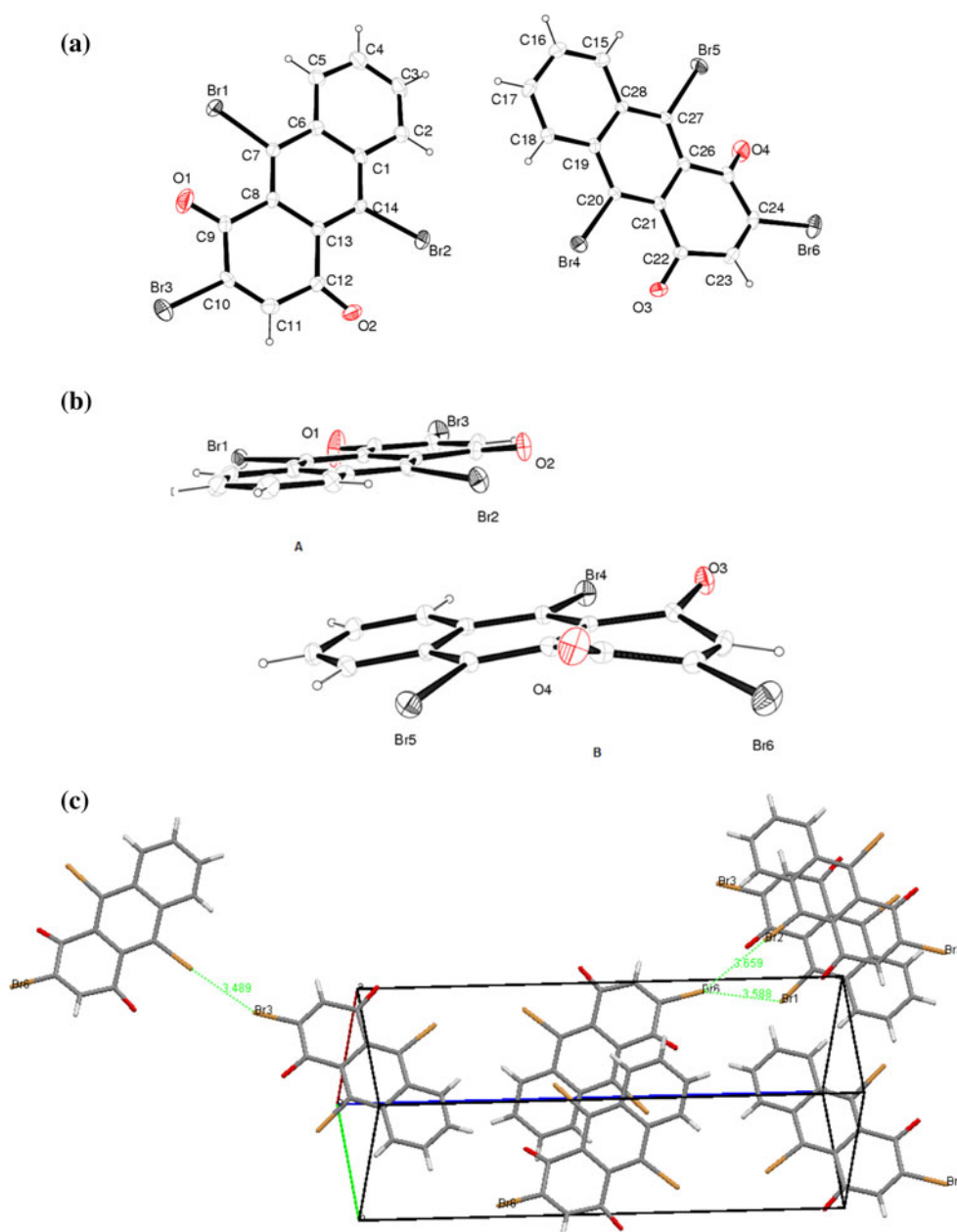


**Fig. 9** Molecular structure of compound **4**

Rigaku R-Axis RAPID-S diffractometer (equipped with a two-dimensional area IP detector). Graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and oscillation scans technique with  $\Delta\omega = 5^\circ$  for one image were used for data collection. The lattice parameters were determined by

the least-squares methods on the basis of all reflections with  $F^2 > 2\sigma(F^2)$ . Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using Crystal Clear (Rigaku/MSC Inc., 2005) software [9]. The structures were solved by direct methods using SHELXS-97 [10] and refined by a full-matrix least-squares procedure using the program SHELXL-97 [10]. H atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance. Crystal data for **4**: C<sub>14</sub>H<sub>5</sub>Br<sub>3</sub>O<sub>2</sub>, crystal system, space group: triclinic,  $P\bar{1}$ ; (no. 2); unit cell dimensions:  $a = 7.6842(2)$ ,  $b = 9.4865(2)$ ,  $c = 19.9388(4) \text{ \AA}$ ,  $\alpha = 78.784(5)$ ,  $\beta = 76.980(5)$ ,  $\gamma = 67.834(4) \text{ \AA}$ ;

**Fig. 10 a, b** Two different perspective views of the molecule **4** in the asymmetric unit. Thermal ellipsoids are shown at 30 % probability level. **c** Unit cell with the Br $\cdots$ Br distances



volume: 1,301.75(7) Å<sup>3</sup>; Z = 2; calculated density: 2.270 g/cm<sup>3</sup>; absorption coefficient: 9.289 mm<sup>-1</sup>; F(000): 840;  $\theta$ -range for data collection 2.3–26.4°; refinement method: full matrix least-square on F<sup>2</sup>; data/parameters: 3,160/344; goodness-of-fit on F<sup>2</sup>: 1.067; final R-indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.0748$ ,  $wR_2 = 0.131$ ; largest diff. peak and hole: 0.617 and -0.684 e Å<sup>-3</sup>.

## Conclusions

In this paper, a novel conformation of 2,9,10-tribromoanthracene-1,4-dione were synthesized and characterized. We assume that origin of the preferred conformation may be attributed order of the events. While the carbonyl groups in the compound **4** form at the first step with the PCC oxidation, the carbonyl groups in the compound **3** form at the second step.

## Supplementary Data

Crystallographic data that were deposited in CSD under CCDC registration number 893848 contain the supplementary crystallographic data for this Letter. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) and are available free of charge upon request to CCDC, 12 Union Road, Cambridge, UK (fax: +441223 336033, e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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