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*Acta Cryst.* (1991). **C47**, 1877–1879

## Synthesis and Structure of a New DDQ Derivative: 3-{{[3,5-Bis(2-pyridyl)-1,2,4-triazol-4-yl]amino}}-5,6-dichloro-2-cyanobenzoquinone

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(Received 8 October 1990; accepted 1 February 1991)

**Abstract.**  $C_{19}H_9Cl_2N_7O_2$ ,  $M_r = 438$ , monoclinic,  $P2_1/n$ ,  $a = 8.500$  (4),  $b = 14.224$  (3),  $c = 17.451$  (10) Å,  $\beta = 91.72$  (2)°,  $V = 2108.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.477$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 2.96$  cm<sup>-1</sup>,  $F(000) = 940$ , room temperature,  $R = 0.0433$ ,  $wR = 0.0513$ , 2916 unique reflections. A new quinoid compound is formed by the substitution of one of the CN groups in 2,3-dichloro-5,6-dicyanobenzoquinone with a 3,5-disubstituted-4-aminotriazole in anhydrous media.

**Introduction.** 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) is well known to act as a powerful acceptor in synthetic oxidative processes (Fatiadi, 1983) and in the formation of highly conductive charge transfer complexes (Mayerle & Torrance, 1981), especially with amino compounds (Ottenberg, Brandon & Browne, 1964). During the course of our investigations upon the complexing properties of 3,5-bis-(2-pyridyl)-4-aminotriazole, we have investigated the possibilities of it acting as a donor in charge transfer complexes especially with DDQ. In rigorously

anhydrous conditions, a new quinoid compound is formed by the substitution of one of the CN groups in DDQ. Indeed the literature reports the substitution of the CN group by an alkoxy or hydroxy group (Middleton, Little, Coffmann & Engelhardt, 1958; Reynolds & Van Allan, 1964; Becker, 1969; Bruni, Tosi & Valle, 1988). To our knowledge, this is the first report of the substitution of a cyano group by an RNH<sub>2</sub> group [ $R = 3,5$ -bis(2-pyridyl)-4-triazolyl]. The compound under study is in fact a new DDQ derivative which can act as a new organic acceptor. These properties are under investigation.

**Experimental.** *Synthesis.* The compound was obtained by mixing equimolecular amounts of dipyridylaminotriazole (dpat) with DDQ in rigorously anhydrous methanol. After standing for 48 h at room temperature, red crystals were recovered. They were air stable and suitable for X-ray analysis. The solvent must be dry to avoid the possibility of substitution of one of the CN ligands by an OH group. Details of the crystal data collection are given in Table 1. The structure was phased and refined by the *SHELX76* program (Sheldrick,

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Table 1. *Experimental details*

|  |  |
|--|--|
| Crystal, dimensions (mm)                     | Red needle, 0.03 × 0.02 × 0.165                        |
| Instrument                                   | Nonius CAD-4   |
| Unit cell                                    | From 25 reflections in the range 2 ≤ θ ≤ 28°           |
| Mode   | ω-2θ   |
| Standards                                    | 130, 133, 211  |
| Range h, k, l                                | -11 → 11, 0 → 18, 0 → 23                               |
| 2θ range (°)                                 | 4-40   |
| Reflections                                  |  |
| Total  | 3870   |
| Observed > 3σ(I)                             | 3681   |
| Unique                                       | 2916   |
| Solution                                     | Direct methods   |
| Weight                                       | w = 1.221[σ <sup>2</sup> (F)] + 0.001767F <sup>2</sup> |
| Parameters refined                           | 339  |
| R, wR  | 0.0433, 0.0513   |
| Goodness of fit                              | 1.194  |
| Maximum shift/e.s.d.                         | 0.01   |
| Δρ <sub>(max,min)</sub> (e Å <sup>-3</sup> ) | 0.241, 0.226   |

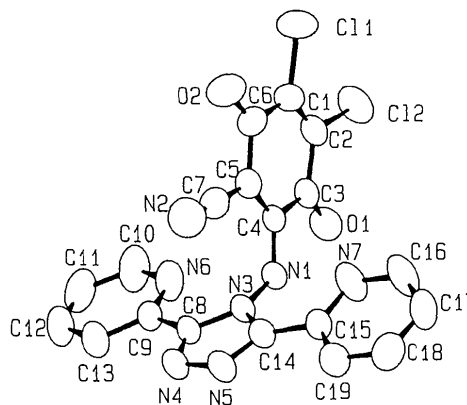


Fig. 1. Atom-numbering scheme and molecular conformation.

Table 2. *Atomic positions (× 10<sup>4</sup>) and isotropic temperature factors (Å<sup>2</sup>)*

|       | x         | y        | z        | B <sub>iso</sub> |
|-------|-----------|----------|----------|------------------|
| Cl(1) | 2912 (1)  | 6203 (1) | 4884 (1) | 6.773            |
| Cl(2) | 4426 (1)  | 4871 (1) | 3622 (1) | 5.90             |
| C(1)  | 2677 (3)  | 5008 (2) | 4875 (2) | 4.269            |
| C(2)  | 3323 (3)  | 4462 (2) | 4354 (2) | 3.958            |
| C(3)  | 3101 (3)  | 3432 (2) | 4370 (1) | 3.368            |
| O(1)  | 3582 (2)  | 2926 (1) | 3876 (1) | 4.734            |
| C(4)  | 2233 (3)  | 3023 (2) | 5033 (1) | 3.043            |
| C(5)  | 1580 (3)  | 3601 (2) | 5556 (1) | 3.592            |
| C(6)  | 1698 (3)  | 4622 (2) | 5491 (1) | 4.329            |
| O(2)  | 1015 (3)  | 5143 (1) | 5911 (2) | 6.642            |
| N(1)  | 2228 (2)  | 2088 (1) | 5002 (1) | 3.096            |
| C(7)  | 686 (3)   | 3286 (2) | 6185 (1) | 4.422            |
| N(2)  | -52 (3)   | 3053 (2) | 6689 (1) | 6.371            |
| N(3)  | 1396 (2)  | 1559 (1) | 5510 (1) | 3.190            |
| N(4)  | 871 (2)   | 627 (1)  | 6467 (1) | 4.313            |
| N(5)  | -428 (2)  | 670 (1)  | 5974 (1) | 4.236            |
| C(8)  | 1961 (3)  | 1157 (1) | 6185 (1) | 3.492            |
| C(9)  | 3530 (3)  | 1292 (2) | 6543 (1) | 3.561            |
| N(6)  | 4415 (3)  | 1971 (2) | 6275 (2) | 5.521            |
| C(10) | 5857 (4)  | 2067 (3) | 6592 (2) | 6.271            |
| C(11) | 6442 (3)  | 1515 (2) | 7177 (1) | 5.010            |
| C(12) | 5492 (4)  | 839 (2)  | 7462 (2) | 5.385            |
| C(13) | 4001 (3)  | 715 (3)  | 7143 (2) | 4.831            |
| C(14) | -106 (3)  | 1224 (2) | 5402 (1) | 3.409            |
| C(15) | -1197 (3) | 1458 (2) | 4762 (1) | 3.705            |
| N(7)  | -690 (3)  | 2025 (2) | 4224 (1) | 5.428            |
| C(16) | -1688 (4) | 2223 (3) | 3640 (2) | 6.696            |
| C(17) | -3178 (4) | 1873 (3) | 3575 (2) | 6.270            |
| C(18) | -3685 (4) | 1307 (3) | 4130 (2) | 6.315            |
| C(19) | -2691 (3) | 1081 (2) | 4745 (2) | 5.478            |
| O(3)  | 2515 (2)  | 809 (1)  | 3837 (1) | 4.098            |
| C(20) | 2160 (5)  | 1117 (3) | 3085 (2) | 5.850            |

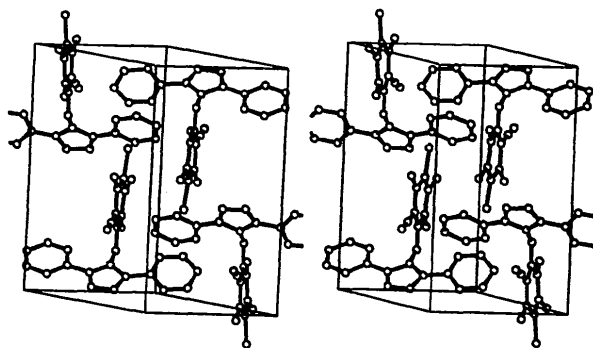


Fig. 2. Stereoscopic view of the unit cell.

deviates slightly from planarity ( $\Delta_{\max} = 0.04 \text{ \AA}$ ), while both O atoms depart from that plane [ $-0.179 (3)$ ,  $-0.128 (2) \text{ \AA}$ ]. Bond distances and angles are in good agreement with those found in analogous structures (Zanotti, Bardi & Delpra, 1980). The molecular configuration is completed by the dpat ligand, with one pyridine and the aminotriazole central group lying in a plane roughly perpendicular to the DDQ ring (interplanar angle =  $93.18^\circ$ ); the second pyridine ring is slightly tilted about the C(8)—C(9) bond; this can be explained by the linkage of two adjacent molecules through two weak hydrogen interactions C(10)—H...Cl(1) =  $2.88 (4) \text{ \AA}$ .

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**Discussion.** The geometry of the molecule is illustrated in Fig. 1 and a stereoview is given in Fig. 2. The ring skeleton of the remaining part of DDQ

\* Lists of structure factors, H-atom parameters, bond lengths and angles and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53971 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1991). **C47**, 1879–1881

## Structure of an Anthracene Derivative

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(Received 12 July 1990; accepted 21 January 1991)

**Abstract.** 7-Methoxy-2-methyl-4,5-dihydroxy-9,10-anthracenedione, physcion,  $C_{16}H_{12}O_5$ ,  $M_r = 284.27$ , orthorhombic,  $P2_12_12_1$ ,  $a = 3.850$  (1),  $b = 23.73$  (3),  $c = 13.667$  (9) Å,  $V = 1249$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.50$  (2),  $D_x = 1.51$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 0.903$  mm<sup>-1</sup>,  $F(000) = 592$ ,  $T = 293$  K, final  $R = 0.0594$  for 1190 unique reflections with  $F > 4\sigma(F)$ . The crystal structure consists of planar molecules which are situated in the  $bc$  plane and form a densely packed arrangement. The structure of physcion differs from both unsubstituted and 1-acetyl-2,4,5,7-tetrahydroxy-9,10-substituted anthracenedione.

**Introduction.** The compound investigated, trivially named physcion, belongs to the anthraquinone derivatives which are known to be secondary metabolites of various microscopic fungi and plants. It is isolated from the filtrate of *mycelia Eurotium (Aspergillus) ropeus*, cultured under stable conditions (Podojil, Sedmera, Vokoun, Betina, Baráthová, Duračková, Horáková & Nemeč, 1979).

**Experimental.** Transparent orange, very thin single crystals were obtained from chloroform; the size of the crystal used was  $0.5 \times 0.5 \times 0.06$  mm.  $D_m$  was measured by flotation. Systematically absent reflections,  $h00$  for  $h$  odd,  $0k0$  for  $k$  odd and  $00l$  for  $l$  odd, were determined from Weissenberg and precession photographs. Accurate unit-cell parameters were

obtained by a least-squares fit of 15 reflections ( $15 < 2\theta < 45^\circ$ ). Intensity data were measured at 193 K on a Syntex  $P2_1$  diffractometer using graphite-monochromated Cu  $K\alpha$  radiation;  $\theta$ - $2\theta$  scan mode with  $(2\theta)_{\text{max}} = 126^\circ$  and the index range  $h$  0/4,  $k$  0/27,  $l$  -14/15. Three standard reflections (060,  $1\bar{1}1$ ,  $1\bar{1}\bar{1}$ ) were measured every 47 reflections, no significant systematic fluctuation was found. 1936 reflections were measured, 1190 of which with  $F_o \geq 4\sigma(F_o)$  were considered observed;  $R_{\text{int}} = 0.073$  for 890 unique reflections before absorption correction. Corrections for absorption effects were made using *DIFABS* (Walker & Stuart, 1983) after isotropic refinement; the maximum and minimum corrections were 1.433 and 0.652, respectively. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1990) and least-squares refined on  $F$  by *SHELX76* (Sheldrick, 1976). A difference map of the partially refined structure gave the positions of all H atoms. Refinement continued on all 235 positional and thermal parameters, anisotropic for non-H atoms and isotropic for H atoms. In the final cycle  $R = 0.059$  and  $wR = 0.061$  were reached, for 1190 observed reflections with weights,  $w$ ,  $w^{-1} = k|\sigma^2(F) + gF^2|$ ,  $k = 0.8294$ ,  $g = 0.00023$ ;  $S = 0.9033$ , max.  $\Delta/\sigma = 0.039$  and max. and min. heights in final  $\Delta\rho$  map +0.23 and -0.26 e Å<sup>-3</sup>. The scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).