

Table 3. Comparison of selected bond lengths (Å) and angles (°) of the ligand and the corresponding nickel chelate, $[\text{Ni}(\text{C}_{12}\text{H}_{15}\text{N}_2\text{S}_2)_2]$ (Sieler *et al.*, 1985)

	$\text{C}_{12}\text{H}_{16}\text{N}_2\text{S}_2$		$[\text{Ni}(\text{C}_{12}\text{H}_{15}\text{N}_2\text{S}_2)_2]$	
	(I)	(II)*	(I)	(II)
S(1)—C(2)	1.675 (6)	1.675 (8)	1.75 (2)	1.73 (1)
S(2)—C(1)	1.639 (6)	1.635 (8)	1.71 (2)	1.71 (1)
N(1)—C(2)	1.408 (7)	1.430 (10)	1.29 (3)	1.34 (2)
N(1)—C(1)	1.365 (7)	1.359 (9)	1.27 (3)	1.29 (2)
N(2)—C(2)	1.335 (7)	1.310 (10)	1.41 (3)	1.35 (2)
S(1)—C(2)—N(1)	119.0 (4)	117.8 (7)	129 (2)	130 (1)
C(2)—N(1)—C(1)	123.3 (5)	123.5 (6)	127 (2)	127 (1)
S(2)—C(1)—N(1)	123.9 (4)	123.3 (6)	134 (2)	132 (1)

* Mean value of the two independent molecules.

As in (I), C(1)—S(2) is about 0.04 Å shorter than C(2)—S(1) which corresponds to distances in thioureas (Kunchur & Truter, 1958; Elcombe & Taylor, 1968; Dias & Truter, 1964) and thioamides (Truter, 1960; Walter, Harto & Voss, 1976).

The C(1)—N(1), C(2)—N(1) and C(2)—N(2) bonds are again intermediate between single and double bonds. C(5)—C(6) (mean value 1.44 Å) is slightly shorter and N(2)—C(5) (mean value 1.52 Å) is longer than the expected values of 1.54 and 1.47 Å (Pauling, 1968). Deviations of this kind are already known from *N*-benzoylthiourea chelates (Fitzl *et al.*, 1977; Knuutila *et al.*, 1982).

The phenyl rings in the two molecules C(71)—C(121) and C(72)—C(122) are tilted by 32.3(3) and 26.8(3)° to the N(11), C(11), S(21) and N(12), C(12), S(22) planes, respectively.

Fig. 3(b) shows the crystal structure of modification (II). Pairs of symmetrically independent molecules are

linked by N—H...S interactions forming dimers. The distances H(12)...S(11) ($1-x, \frac{1}{2}+y, 1-z$) and H(11)...S(12) ($1-x, y-\frac{1}{2}, 1-z$) are 2.42 and 2.52 Å respectively.

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Structure of 2,4,5,7-Tetramethyl-9,10-phenanthroquinone

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Abstract. $\text{C}_{18}\text{H}_{16}\text{O}_2$, $M_r = 264.32$, monoclinic, $I2/a$, $a = 19.389$ (3), $b = 8.708$ (1), $c = 17.554$ (3) Å, $\beta = 112.11$ (1)°, $V = 2745.8$ (8) Å³, $Z = 8$, $D_x = 1.279$ g cm⁻³, $\text{Mo } K\alpha$, $\lambda = 0.7093$ Å, $\mu = 0.766$ cm⁻¹,

$F(000) = 1120$, $T = 298$ K, $R = 0.046$ for 1889 reflections with $I > 2.5\sigma(I)$. The repulsion between the two methyl groups at C(4) and C(5) and the electrostatic repulsion from the orthoquinone functionality cause a severe deviation from planarity for the phenanthroquinone skeleton. The torsional angle C(4)—C(12)—

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C(13)–C(5) [39.9°] is the largest known in a phenanthrene derivative. Though not required crystallographically, C₁₈H₁₆O₂ virtually has C₂ molecular symmetry.

Introduction. Recent interest in studies of the stereo-electronic effect (Kirby, 1983; Deslongchamps, 1983) has turned our attention to the synthesis of compounds such as 1,3,6,8- and 2,4,5,7-tetramethylphenanthrene and the corresponding 9,10-phenanthroquinones in the hope of understanding the effect of steric hindrance at C(4) and C(5) on physical properties, e.g. the UV absorption, and the possible consequences for the chemistry of these compounds. The correlations between the crystal and molecular structures and the spectroscopic data are expected to be rewarding in the rationalization of this distorted aromatic system.

Experimental. The novel 2,4,5,7-tetramethyl-9,10-phenanthroquinone was prepared from the oxidation of 2,4,5,7-tetramethylphenanthrene (Blackburn, Loader & Timmons, 1968) using chromic acid in acetic acid (Graebe, 1873). Recrystallization from methanol gave orange prisms, m.p. 468–469 K (dec.); ¹H NMR (CDCl₃) δ = 2.25 (6H, s), 2.40 (6H, s), 7.33 (2H, br. s), 7.67 (2H, br. s); IR (KBr) cm⁻¹, 1620, 1680; MS(*m/e*) 264 (5%, M⁺), 236 (28%), 221 (16%), 193 (75%), 178 (45%), 165 (28%), 51 (52%), 39 (100%); UV (hexane) nm(ε), 220 (5800), 253 (4400), 301 (800); calculated elemental analysis C: 81.8%, H: 6.06%, found C: 81.7%, H: 6.14%.

Nonius CAD-4 diffractometer, 2 < 2θ < 60°, Mo Kα, ω–2θ scan with speeds from 0.9–6.7° min⁻¹, (0.7 + 0.35 tanθ)° around maximum, h –27 to 25, k 0 to 12, l 0 to 22, 25 reflections (20 < 2θ < 30°) used for measuring lattice constants. Data crystal size ca 0.2 × 0.3 × 0.4 mm. Three standard reflections (811, $\bar{8}\bar{1}\bar{1}$ and $\bar{8}\bar{1}\bar{1}$) after every 7200 s, no decay or decomposition found. 3995 unique reflections measured, 1889 observed with I > 2.5σ(I). Structure solved by direct methods with MULTAN (Main, Fiske,

Hull, Lessinger, Germain, Declercq & Woolfson, 1982). H atoms found in difference Fourier synthesis. No absorption correction applied. Structure refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$, w from counting statistics only. Calculations carried out with anisotropic O, C, and isotropic H. Scattering factors from *International Tables for X-ray Crystallography* (1974). Final R = 0.046 and wR = 0.034. Max. Δ/σ for the last cycle 0.5. Max. and min. peak heights in final difference map 0.48 and –0.50 e Å⁻³. Computations carried out on a VAX 780 with the NRCC package (Larson, Lee, Le Page & Gabe, 1986).

Discussion. An ORTEP drawing (Johnson, 1965) of the molecule is shown in Fig. 1. Final atomic coordinates are given in Table 1, bond lengths and angles in Table 2, and torsional angles in Table 3.*

There is evidence that the two methyl groups at C(4) and C(5) cause steric repulsion. The repulsion, in turn, influences the electronic properties of the phenanthroquinone chromophore. An isomer of the title compound has been similarly prepared, namely 1,3,6,8-tetramethyl-9,10-phenanthroquinone, whose crystals are golden needles. The blue shift in UV for the title compound is indicative that this chromophore is more strained. The lower stretching frequencies for the orthoquinone functionality of the title compound, as revealed by IR, result from a loss of the planarity of phenanthrene skeleton. The molecular structure of the title compound corresponds very well to a loss of planarity. The features are best seen *via* the torsional angles.

Similar molecular structures with substituents at C(4) and C(5) all reveal a large torsional angle C(4)–C(12)–C(13)–C(5): namely decachlorophenanthrene (DCP) 27.9° (Herbstein, Kapon & Merksamer, 1976), 1,10-dichloro-3,8-dimethyl-4,7-phenanthroline (DCDMP) 20.5° (Herbstein, Kapon & Rabinovich, 1972), and 2,4,5,7-tetramethylphenanthrene (TMP) 32.7° (Ho, Hsu, Hwang & Liu, 1986). However, the torsional angle of the title compound (39.9°) is the largest known for a phenanthrene derivative. On the other hand, DCP, DCDMP and TMP have C(14)–C(9)–C(10)–C(11) torsional angles of 5.7, 11.6 and 11.0°, respectively. Nevertheless, this angle is 35.5° in the title compound. DCP, DCDMP and TMP each have a simple double bond at C(9)–C(10), which is apparently effective for a resonance through all the conjugated double bonds, as compared to the single-bond (sp²–sp²) character of C(9)–C(10) in the title compound.

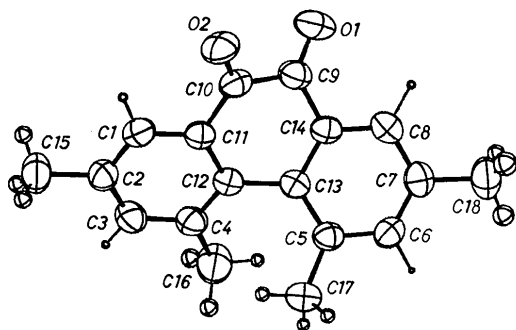


Fig. 1. ORTEP drawing (Johnson, 1965) of 2,4,5,7-tetramethyl-9,10-phenanthroquinone with the atomic numbering sequence.

* Lists of structure factors, thermal parameters, H-atom coordinates, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43254 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The O(1)–C(9)–C(10)–O(2) torsional angle of 27.4° in the title compound is also surprisingly large. For *o*-benzoquinone (Macdonald & Trotter, 1973) the torsional angle for the orthoquinone functionality O–C–C–O is only 2.4°, indicative of a resonance through all conjugated double bonds and of the limited steric effect of the two nearby O atoms. It is believed that in the title compound, the 9,10-orthoquinone functionality, as a pair of dipoles, still prefers the two O atoms to point away from each other due to electrostatic repulsion. Hence, the torsional angle O(1)–C(9)–C(10)–O(2) is large.

Table 1. Final fractional coordinates of non-H atoms for 2,4,5,7-tetramethylphenanthroquinone

$$B_{\text{iso}} = 8\pi^2/3 \sum U_{ii}$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}(\text{Å}^2)$
O(1)	0.1667 (1)	−0.1236 (2)	0.1297 (1)	6.7 (1)
O(2)	0.0742 (1)	0.1000 (2)	0.0311 (1)	5.4 (1)
C(1)	−0.0341 (2)	0.2002 (3)	0.0957 (2)	4.0 (2)
C(2)	−0.0825 (1)	0.2458 (3)	0.1325 (2)	4.2 (1)
C(3)	−0.0560 (2)	0.2432 (3)	0.2171 (2)	4.4 (2)
C(4)	0.0171 (1)	0.2078 (3)	0.2671 (2)	4.0 (1)
C(5)	0.1930 (1)	0.2302 (3)	0.3452 (2)	3.7 (1)
C(6)	0.2657 (2)	0.1793 (3)	0.3883 (2)	4.1 (1)
C(7)	0.2973 (1)	0.0581 (3)	0.3627 (2)	4.0 (1)
C(8)	0.2564 (2)	−0.0095 (3)	0.2885 (2)	4.1 (2)
C(9)	0.1474 (2)	−0.0138 (3)	0.1589 (2)	4.1 (1)
C(10)	0.0848 (1)	0.0900 (3)	0.1033 (2)	3.8 (1)
C(11)	0.0394 (1)	0.1638 (3)	0.1435 (1)	3.5 (1)
C(12)	0.0680 (1)	0.1770 (3)	0.2295 (1)	3.4 (1)
C(13)	0.1489 (1)	0.1497 (3)	0.2754 (1)	3.3 (1)
C(14)	0.1840 (1)	0.0378 (3)	0.2446 (2)	3.5 (1)
C(15)	−0.1624 (2)	0.2863 (5)	0.0817 (3)	5.8 (2)
C(16)	0.0346 (2)	0.1877 (6)	0.3577 (2)	6.0 (2)
C(17)	0.1704 (2)	0.3792 (4)	0.3724 (2)	5.0 (2)
C(18)	0.3761 (2)	0.0059 (5)	0.4130 (3)	5.8 (2)

Table 2. Bond lengths (Å) and angles (°) for 2,4,5,7-tetramethylphenanthroquinone

			Average
O(1)–C(9)	1.208 (3)	O(2)–C(10)	1.207 (3)
C(1)–C(2)	1.382 (4)	C(7)–C(8)	1.377 (4)
C(1)–C(11)	1.392 (4)	C(8)–C(14)	1.385 (4)
C(2)–C(3)	1.377 (4)	C(6)–C(7)	1.377 (4)
C(2)–C(15)	1.510 (4)	C(7)–C(18)	1.518 (4)
C(3)–C(4)	1.392 (4)	C(5)–C(6)	1.397 (4)
C(4)–C(12)	1.403 (4)	C(5)–C(13)	1.392 (4)
C(4)–C(16)	1.507 (4)	C(5)–C(17)	1.503 (4)
C(9)–C(10)	1.533 (4)		
C(9)–C(14)	1.471 (4)	C(10)–C(11)	1.469 (4)
C(11)–C(12)	1.403 (3)	C(13)–C(14)	1.407 (4)
C(12)–C(13)	1.489 (3)		
			Average
C(2)–C(1)–C(11)	120.3 (3)	C(7)–C(8)–C(14)	120.1 (3)
C(1)–C(2)–C(3)	117.1 (3)	C(6)–C(7)–C(8)	117.8 (3)
C(1)–C(2)–C(15)	121.2 (3)	C(8)–C(7)–C(18)	121.2 (3)
C(3)–C(2)–C(15)	121.6 (3)	C(6)–C(7)–C(18)	120.9 (3)
C(2)–C(3)–C(4)	124.2 (3)	C(5)–C(6)–C(7)	123.3 (3)
C(3)–C(4)–C(12)	118.4 (2)	C(6)–C(5)–C(13)	118.5 (3)
C(3)–C(4)–C(16)	117.5 (3)	C(6)–C(5)–C(17)	117.2 (3)
C(12)–C(4)–C(16)	123.8 (3)	C(13)–C(5)–C(17)	123.9 (3)
O(1)–C(9)–C(10)	119.5 (3)	O(2)–C(10)–C(9)	119.5 (2)
O(1)–C(9)–C(14)	124.7 (3)	O(2)–C(10)–C(11)	125.2 (3)
C(10)–C(9)–C(14)	115.6 (2)	C(9)–C(10)–C(11)	115.2 (2)
C(1)–C(11)–C(10)	118.2 (2)	C(8)–C(14)–C(9)	118.4 (2)
C(1)–C(11)–C(12)	122.1 (2)	C(8)–C(14)–C(13)	121.8 (3)
C(10)–C(11)–C(12)	119.2 (2)	C(9)–C(14)–C(13)	119.2 (2)
C(4)–C(12)–C(11)	117.3 (2)	C(5)–C(13)–C(14)	117.5 (2)
C(4)–C(12)–C(13)	124.1 (2)	C(5)–C(13)–C(12)	124.7 (2)
C(11)–C(12)–C(13)	118.5 (2)	C(12)–C(13)–C(14)	117.8 (2)

Table 3. Torsional angles (°) for 2,4,5,7-tetramethylphenanthroquinone

			Average
C(11)–C(1)–C(2)–C(3)	−4.1	C(6)–C(7)–C(8)–C(14)	−4.2
C(11)–C(1)–C(2)–C(15)	179.8	C(18)–C(7)–C(8)–C(14)	178.6
C(2)–C(1)–C(11)–C(10)	169.2	C(7)–C(8)–C(14)–C(9)	167.8
C(2)–C(1)–C(11)–C(12)	−2.5	C(7)–C(8)–C(14)–C(13)	−3.0
C(1)–C(2)–C(3)–C(4)	4.4	C(5)–C(6)–C(7)–C(8)	4.0
C(15)–C(2)–C(3)–C(4)	−179.6	C(5)–C(6)–C(7)–C(18)	−178.7
C(2)–C(3)–C(4)–C(12)	2.0	C(13)–C(5)–C(6)–C(7)	3.4
C(2)–C(3)–C(4)–C(16)	−171.4	C(17)–C(5)–C(6)–C(7)	−170.0
C(3)–C(4)–C(12)–C(11)	−8.4	C(6)–C(5)–C(13)–C(14)	−10.3
C(3)–C(4)–C(12)–C(13)	175.0	C(6)–C(5)–C(13)–C(12)	171.7
C(16)–C(4)–C(12)–C(11)	164.5	C(17)–C(5)–C(13)–C(14)	162.6
C(16)–C(4)–C(12)–C(13)	−12.1	C(17)–C(5)–C(13)–C(12)	−15.4
O(1)–C(9)–C(10)–O(2)	−27.4		
O(1)–C(9)–C(10)–C(11)	149.3	C(14)–C(9)–C(10)–O(2)	147.8
C(14)–C(9)–C(10)–C(11)	−35.5		
O(1)–C(9)–C(14)–C(8)	20.1	O(2)–C(10)–C(11)–C(1)	24.6
O(1)–C(9)–C(14)–C(13)	−168.8	O(2)–C(10)–C(11)–C(12)	−163.4
C(10)–C(9)–C(14)–C(8)	−154.8	C(9)–C(10)–C(11)–C(1)	−151.8
C(10)–C(9)–C(14)–C(13)	16.3	C(9)–C(10)–C(11)–C(12)	20.1
C(1)–C(11)–C(12)–C(4)	8.8	C(5)–C(13)–C(14)–C(8)	10.4
C(1)–C(11)–C(12)–C(13)	−174.4	C(12)–C(13)–C(14)–C(8)	−171.5
C(10)–C(11)–C(12)–C(4)	−162.8	C(5)–C(13)–C(14)–C(9)	−160.4
C(10)–C(11)–C(12)–C(13)	14.0	C(12)–C(13)–C(14)–C(9)	17.6
C(4)–C(12)–C(13)–C(5)	−39.9		
C(4)–C(12)–C(13)–C(14)	142.1	C(11)–C(12)–C(13)–C(5)	143.5
C(11)–C(12)–C(13)–C(14)	−34.5		

The overcrowdedness of the title compound also shows an elongation of the bond C(12)–C(13), *i.e.* from 1.457 Å in phenanthrene (Kay, Okaya & Cox, 1971) to 1.490 Å in the title compound. Seemingly, the same pattern follows for DCP and DCDMP as well.

The thermal parameters are such that the phenanthrene C atoms are more restricted in motion, whereas the terminal methyl C atoms and the quinone O atoms are less restricted. The thermal parameters of H atoms are also associated with two groups: the more-restricted phenanthrene H atom and the less-restricted methyl H atom. The steric hindrance, which would tend to force the two methyl groups of C(4) and C(5) together and reduce thermal motion, could partly be released because of the 9,10 orthoquinone functionality. Hence, no abnormal thermal parameters are seen for C(16) and C(17) as well as the attached H atoms.

Though not required crystallographically, the title compound virtually has C_2 molecular symmetry, not including the methyl H atoms, as revealed by structural parameters which are averaged on the basis of chemical equivalence.

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Structure of (–)-Canadinium (+)-10-Camphorsulfonate

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Abstract. $C_{20}H_{22}NO_4^+ \cdot C_{10}H_{15}O_4S^-$, $M_r = 571.69$, orthorhombic, $P2_12_12_1$, $a = 11.231$ (2), $b = 32.025$ (5), $c = 7.584$ (1) Å, $V = 2727.8$ (10) Å³, $Z = 4$, $D_x = 1.392$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 0.1764$ mm⁻¹, $F(000) = 1216$, room temperature. Final $R = 0.055$ for 1440 unique observed reflections. The absolute configuration of (–)-canadine was obtained in relation to that of (+)-10-camphorsulfonic acid and also by use of the anomalous-dispersion effects of the S and the O atoms. In the crystal of the title compound, (–)-canadine, (–)-(13a*S*)-5,6,13,13a-tetrahydro-9,10-dimethoxy-2,3-methylenedioxy-8*H*-dibenzo[*a,g*]quinolizine, takes a *trans* configuration in the quinolizidine ring. The distance between the N atom of the canadinium ion and one O atom in the sulfonate group of the camphorsulfonate ion, 2.683 Å, indicates that these two are connected by a hydrogen bond.

Introduction. (–)-Canadine, which belongs to the protoberberine-type alkaloids, was isolated from several *Corydalis* plants (Papaveraceae), *i.e.* *Corydalis cheilanthifolia*, *C. ophiocarpa* and *C. ternata*, and its structure was determined to be that of tetrahydroberberine (Manske & Holmes, 1954; Boit, 1961). Studies on the crystal-structure analysis of proto-

berberine-type alkaloids showed that there are a few alkaloid salts which have the *B/C-cis* ring-juncture configuration (Shimanouchi, Sasada, Ihara & Kametani, 1969; Shimanouchi, Sasada, Kametani & Ihara, 1970). However, there have been no detailed studies on these salts with the *B/C-trans* juncture configuration. (–)-Canadinium (+)-10-camphorsulfonate should be obtainable in the process of optical resolution of racemic (±)-canadine as a diastereomeric salt. We prepared this compound, which was, by spectroscopic studies, to have the *trans* juncture configuration, and used this to determine the crystal structure. If the crystal structure is determined, the absolute configuration of (–)-canadine could be obtained in relation to that of (+)-10-camphorsulfonic acid. Until now we have a report suggesting the absolute configuration of (–)-canadine by circular dichroism (Snatzke, Hrubek, Hruban, Horeau & Šantavý, 1970).

Experimental. Compound prepared by reaction of stoichiometric quantities of constituent molecules in acetic acid. Crystal specimens obtained from dimethyl sulfone solutions. Crystal 0.1 × 0.3 × 0.5 mm, thin rectangular plate. Rigaku AFC-5 four-circle diffrac-