

| | | | |
|------------------|-----------|-------------------|-----------|
| C(5)—O(1)—C(11) | 109.9 (3) | C(5)—C(10)—C(9) | 110.4 (2) |
| C(9)—O(2)—C(14) | 118.1 (2) | C(5)—C(10)—C(25) | 111.9 (3) |
| C(15)—O(4)—C(16) | 62.3 (2) | C(9)—C(10)—C(25) | 105.2 (2) |
| C(1)—O(5)—C(23) | 118.1 (2) | O(1)—C(11)—C(7) | 102.2 (2) |
| C(2)—O(7)—C(26) | 116.4 (2) | O(1)—C(11)—C(12) | 109.3 (3) |
| O(5)—C(1)—C(2) | 109.4 (2) | O(1)—C(11)—C(13) | 108.6 (3) |
| O(5)—C(1)—C(10) | 106.1 (2) | C(7)—C(11)—C(12) | 112.3 (3) |
| C(2)—C(1)—C(10) | 116.1 (3) | C(7)—C(11)—C(13) | 116.6 (3) |
| O(7)—C(2)—C(1) | 109.8 (2) | C(12)—C(11)—C(13) | 107.6 (3) |
| O(7)—C(2)—C(3) | 110.7 (3) | O(2)—C(14)—O(3) | 126.4 (3) |
| C(1)—C(2)—C(3) | 110.4 (3) | O(2)—C(14)—C(15) | 112.2 (3) |
| C(2)—C(3)—C(4) | 116.1 (3) | O(3)—C(14)—C(15) | 121.3 (3) |
| C(3)—C(4)—C(5) | 111.3 (3) | O(4)—C(15)—C(14) | 118.6 (3) |
| C(3)—C(4)—C(28) | 112.8 (3) | O(4)—C(15)—C(16) | 59.1 (2) |
| C(5)—C(4)—C(28) | 116.4 (3) | C(14)—C(15)—C(16) | 121.4 (3) |
| O(1)—C(5)—C(4) | 106.4 (2) | O(4)—C(16)—C(15) | 58.6 (2) |
| O(1)—C(5)—C(6) | 104.1 (2) | O(4)—C(16)—C(17) | 116.6 (3) |
| O(1)—C(5)—C(10) | 106.0 (2) | C(15)—C(16)—C(17) | 119.4 (3) |
| C(4)—C(5)—C(6) | 114.3 (3) | C(16)—C(17)—C(18) | 118.3 (3) |
| C(4)—C(5)—C(10) | 115.6 (2) | C(16)—C(17)—C(22) | 122.2 (3) |
| C(6)—C(5)—C(10) | 109.5 (2) | C(18)—C(17)—C(22) | 119.5 (3) |
| C(5)—C(6)—C(7) | 99.4 (3) | C(17)—C(18)—C(19) | 119.4 (4) |
| C(6)—C(7)—C(8) | 107.8 (3) | C(18)—C(19)—C(20) | 121.2 (4) |
| C(6)—C(7)—C(11) | 100.6 (2) | C(19)—C(20)—C(21) | 119.4 (4) |
| C(8)—C(7)—C(11) | 114.7 (3) | C(20)—C(21)—C(22) | 120.3 (4) |
| C(7)—C(8)—C(9) | 115.7 (3) | C(17)—C(22)—C(21) | 120.2 (3) |
| O(2)—C(9)—C(8) | 108.1 (2) | O(5)—C(23)—O(6) | 124.2 (3) |
| O(2)—C(9)—C(10) | 110.7 (2) | O(5)—C(23)—C(24) | 111.1 (4) |
| C(8)—C(9)—C(10) | 114.6 (3) | O(6)—C(23)—C(24) | 124.7 (3) |
| C(1)—C(10)—C(5) | 108.0 (2) | O(7)—C(26)—O(8) | 123.8 (3) |
| C(1)—C(10)—C(9) | 110.0 (3) | O(7)—C(26)—C(27) | 111.9 (3) |
| C(1)—C(10)—C(25) | 111.3 (2) | O(8)—C(26)—C(27) | 124.4 (3) |

Intensities were measured with a scan width of $(0.55 + 0.35\tan\theta)^\circ$ and a scan rate of $1.0-8.24^\circ \text{ min}^{-1}$, extended 25% on each side for background measurement. $\sigma^2(I)$ was calculated as $S + 4(B_1 + B_2) + (0.04S)^2$, where S = scan, B_1 and B_2 = background counts. The structure was solved by direct methods using the program RANTAN (Yao, 1981) and refined by block and full-matrix least-squares calculations on F . Anisotropic displacement parameters were refined for non-H atoms. All H atoms were located from difference maps, included in the structure-factor calculations and refined with fixed isotropic temperature factors (5.0 \AA^2). All calculations were performed on a PDP 11/44 computer with the Enraf-Nonius CAD-4 SDP package (Enraf-Nonius, 1985).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71272 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR0163].

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Ethylenediamine-*N,N'*-dimethyl-*N,N'*-2,2'-di-6-*tert*-butyl-1,4-benzoquinone

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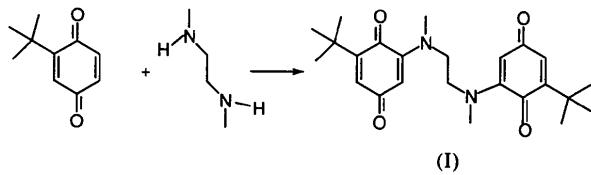
(Received 18 May 1994; accepted 28 September 1994)

Abstract

The title molecule, C₂₄H₃₂N₂O₄, is crystallographically centrosymmetric with the two benzoquinone rings parallel. Benzoquinone rings generally have a flattened envelope conformation with localized double bonds. The presence of two substituents on one side of the benzoquinone ring leads to an unsymmetrical degree of π -electron delocalization which is most significant along N1—C1=C2—C3. The *tert*-butyl groups are *anti* to the methyl groups which enables an effective three-dimensional packing of the molecules. The molecular structure is dominated by van der Waals interactions and an intermolecular hydrogen bond [O1···H4a = 2.46 Å].

Comment

As a part of our ongoing studies of the coupling reactions between amines and various quinones, we have prepared the title compound, (I), by the reaction of *tert*-butylbenzoquinone with *N,N'*-dimethylethylenediamine. To our knowledge, this is the first example of a 2:1 quinone-amine adduct characterized crystallographically. There are few structures of quinone-amine adducts reported in the literature; all have only one quinone moiety in the molecule and either two (Schmalle, Bürgi & Rüedi, 1991; Retting & Trotter, 1975; Kulpe, 1970) or four (Bock, Ruppert, Nather & Havlas, 1991) amine substituents. The X-ray analysis confirms the quinoid structure of the product and the regioselectivity of the reaction. The full account of spectroscopic and kinetic data will be published elsewhere (Raptova & Horak, 1995).



The molecule has a centre of inversion in the middle of the C7—C7a bond with the two quinone rings being parallel. Views of the molecule showing the labeling scheme of the non-H atoms and the packing of the molecules in the unit cell can be seen in Figs. 1 and 2. The mean deviations of two O atoms from the plane defined by C1, C2, C3 and C4 [plane A, mean deviation = 0.012(4) Å] are −0.019 Å for O1 and −0.995 Å for O2; thus the ring has a flattened envelope conformation. The C6=O2 bond is 0.022 Å longer than the C3=O1 bond which indicates a higher degree of delocalization in the substituted part of the quinone ring. A certain degree of delocalization of

C=C π electrons in the unsubstituted part of the quinone ring and resonance with the amino group, which was observed in 6-pentyl-2,5-bis(phenethylamino)-1,4-benzoquinone (Schmalle, Bürgi & Rüedi, 1991), is also observed in the present structure. The C1=C2 double bond is lengthened to 1.364(2) Å while the C2—C3 and C1—N1 single bonds are shortened to 1.431(2) and 1.358(2) Å, respectively. The N1 and C10 atoms do not lie exactly in the plane A, but are displaced by 0.120 and −0.014 Å from the plane, respectively. The C—C bond distances of the *tert*-butyl groups have standard values but the C11—C10—C12 angle [110.07(12) $^\circ$] is smaller than usual, which seems to reduce the intermolecular crowding of the *tert*-butyl groups (Iimura, Sakurai, Ohno, Asahi & Isono, 1983). The packing of the molecules in the crystal is dominated by van der Waals interactions and intermolecular hydrogen bonds [O1...H4aⁱ 2.46 Å; symmetry code: (i) $-x, -y + 1, -z + 2$] (Fig. 2).

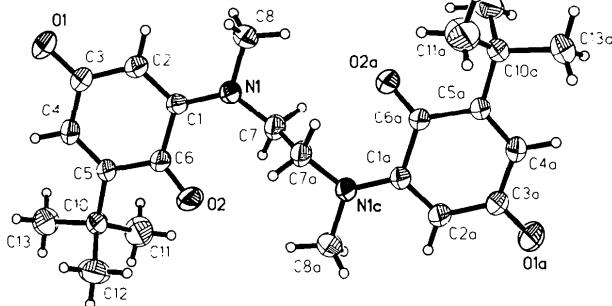


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids and the labeling scheme.

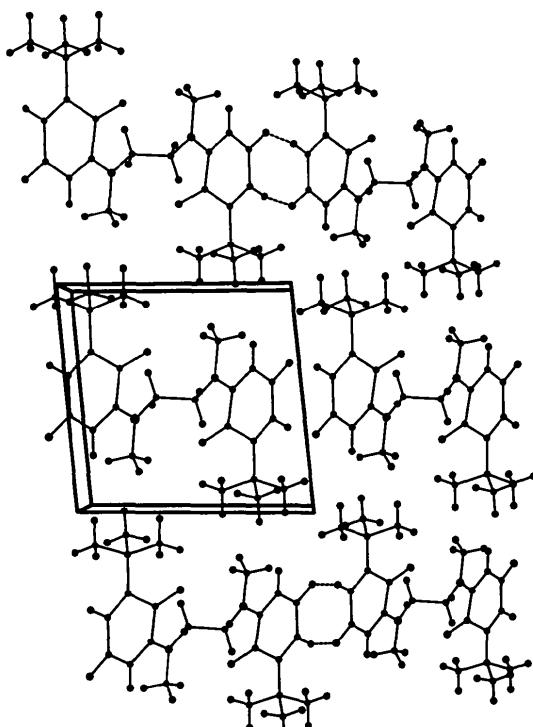


Fig. 2. Molecular packing in the unit cell viewed down the a axis. Dashed lines indicate hydrogen bonds.

Experimental

To a well stirred ethanol solution of *tert*-butylbenzoquinone (10 mmol) was added dimethylethylenediamine (5 mmol) and the reaction mixture was stirred at room temperature for 24 h. The fine precipitate was filtered and recrystallization from hot ethanol in a Dewar flask yielded dark red crystals.

Crystal data

$C_{24}H_{32}N_2O_4$
 $M_r = 412.52$
Triclinic
 $P\bar{1}$
 $a = 6.1970(10)$ Å
 $b = 9.348(2)$ Å
 $c = 9.713(2)$ Å
 $\alpha = 83.90(1)$ $^\circ$
 $\beta = 84.97(1)$ $^\circ$
 $\gamma = 85.85(2)$ $^\circ$
 $V = 556.2(2)$ Å³
 $Z = 1$
 $D_x = 1.232$ Mg m^{−3}

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
 $\theta = 6\text{--}17$ $^\circ$
 $\mu = 0.084$ mm^{−1}
 $T = 293(2)$ K
Transparent block
 $0.5 \times 0.3 \times 0.3$ mm
Red

Data collection

Siemens P4/RA four-circle diffractometer
 ω scans
Absorption correction:
none
3732 measured reflections
2949 independent reflections
2148 observed reflections
[$I > 2\sigma(I)$]

$R_{\text{int}} = 0.0256$
 $\theta_{\text{max}} = 29.03$ $^\circ$
 $h = -1 \rightarrow 8$
 $k = -12 \rightarrow 12$
 $l = -13 \rightarrow 13$
3 standard reflections monitored every 97 reflections
intensity decay: 2%

Refinement

Refinement on F^2
 $R(F) = 0.0531$
 $wR(F^2) = 0.1372$
 $S = 1.054$

$(\Delta/\sigma)_{\text{max}} = 0.014$
 $\Delta\rho_{\text{max}} = 0.308$ e Å^{−3}
 $\Delta\rho_{\text{min}} = -0.233$ e Å^{−3}
Extinction correction: none

2941 reflections
136 parameters
H atoms riding, C—H = 0.96 Å
 $w = 1/[\sigma^2(F_o^2) + (0.0731P)^2 + 0.1064P]$
where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1067). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} |
|-----|------------|--------------|--------------|------------------------|
| C1 | 0.6554 (2) | 0.46352 (14) | 0.72286 (14) | 0.0344 (3) |
| C2 | 0.5261 (2) | 0.37590 (15) | 0.8102 (2) | 0.0407 (3) |
| C3 | 0.3320 (2) | 0.4311 (2) | 0.8827 (2) | 0.0412 (3) |
| C4 | 0.2790 (2) | 0.5885 (2) | 0.87007 (15) | 0.0382 (3) |
| C5 | 0.3934 (2) | 0.68110 (14) | 0.78238 (14) | 0.0333 (3) |
| C6 | 0.5691 (2) | 0.61730 (14) | 0.68736 (15) | 0.0399 (3) |
| O1 | 0.2124 (2) | 0.35140 (14) | 0.9597 (2) | 0.0660 (4) |
| O2 | 0.6329 (3) | 0.68388 (14) | 0.57901 (14) | 0.0756 (5) |
| N1 | 0.8482 (2) | 0.41617 (13) | 0.66042 (13) | 0.0429 (3) |
| C7 | 1.0069 (2) | 0.5047 (2) | 0.57713 (14) | 0.0389 (3) |
| C8 | 0.9209 (3) | 0.2649 (2) | 0.6892 (2) | 0.0552 (5) |
| C10 | 0.3479 (2) | 0.84453 (14) | 0.76812 (15) | 0.0386 (3) |
| C11 | 0.5585 (2) | 0.91824 (14) | 0.77722 (15) | 0.0667 (6) |
| C12 | 0.2509 (2) | 0.89601 (14) | 0.62999 (15) | 0.0610 (5) |
| C13 | 0.1859 (3) | 0.8905 (2) | 0.8861 (2) | 0.0601 (5) |

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|-----------|-------------|-----------------------|-------------|
| C1—N1 | 1.358 (2) | C5—C10 | 1.527 (2) |
| C1—C2 | 1.364 (2) | C6—O2 | 1.214 (2) |
| C1—C6 | 1.512 (2) | N1—C8 | 1.458 (2) |
| C2—C3 | 1.431 (2) | N1—C7 | 1.464 (2) |
| C3—O1 | 1.236 (2) | C7—C7 ¹ | 1.520 (3) |
| C3—C4 | 1.478 (2) | C10—C13 | 1.531 (2) |
| C4—C5 | 1.343 (2) | C10—C11 | 1.533 (2) |
| C5—C6 | 1.497 (2) | C10—C12 | 1.535 (2) |
| N1—C1—C2 | 123.04 (12) | O2—C6—C1 | 119.96 (12) |
| N1—C1—C6 | 119.41 (11) | C5—C6—C1 | 118.89 (11) |
| C2—C1—C6 | 117.39 (12) | C1—N1—C8 | 118.39 (12) |
| C1—C2—C3 | 121.71 (13) | C1—N1—C7 | 126.67 (11) |
| O1—C3—C2 | 121.74 (14) | C8—N1—C7 | 114.58 (12) |
| O1—C3—C4 | 119.26 (13) | N1—C7—C7 ¹ | 111.0 (2) |
| C2—C3—C4 | 118.94 (12) | C5—C10—C13 | 110.67 (12) |
| C5—C4—C3 | 122.69 (12) | C5—C10—C11 | 109.68 (11) |
| C4—C5—C6 | 116.92 (12) | C13—C10—C11 | 107.62 (14) |
| C4—C5—C10 | 124.52 (12) | C5—C10—C12 | 110.74 (12) |
| C6—C5—C10 | 118.47 (11) | C13—C10—C12 | 107.99 (13) |
| O2—C6—C5 | 120.99 (12) | C11—C10—C12 | 110.07 (12) |

Symmetry code: (i) 2 - *x*, 1 - *y*, 1 - *z*.

Methyl H atoms were located using difference Fourier syntheses with toroidal averaging and were included in subsequent calculations as a group with idealized tetrahedral geometry riding on the methyl C atom. The positions of all other H atoms were calculated and constrained to ride on their respective C atoms.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

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7,7-Dibromo-3-dibromomethylene-2,2-dimethylnorbornan-1-ol

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Abstract

The X-ray structure of the title compound, C₁₀H₁₂Br₄O, which is a by-product of 3,3-dibromocamphor bromination, confirms the structure predicted on the basis of spectroscopic data. The geometry of the molecular skeleton (a six-membered boat and two five-membered envelopes) does not differ significantly from those of other norbornane derivatives (norbornane is bicyclo[2.2.1]heptane). O—H· · · Br intermolecular hydrogen bonds link the molecules to form infinite chains along the [100] direction. The pattern of the non-bonding contact distances can be used for discussing similar interactions in the corresponding carbocationic intermediates of the bromination process.