

2.452 (2) Å for the second hydrogen bond. In the structure of (1) the opposite is observed, O(11)—O(23) [2.456 (4) Å] being shorter than O(13)—O(21) [2.483 (4) Å].

The C—C distances in each succinate residue in (1) are internally equivalent within the standard deviations, but there is a difference between the two residues. The mean C—C distance in the first residue is 1.510 compared to 1.522 Å in the second. The same mean C—C distance in (2) is 1.5150 Å. The longer mean C—C distance in the second residue in (1) can be explained by the observation that O(24) in this residue is involved in the shortest N—O hydrogen bond [2.773 (5) Å] in (1), thereby stretching the succinate entity.

The dimensions of the cations are listed in Table 3. The three N—C distances are equivalent within the standard deviations. The C—C distances for the second residue in (1) and (2) are equivalent, while the C—C distance for the first residue is slightly smaller.

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The Structure of a Benzoquinone Diimine *N,N'*-Dioxide Derivative

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Abstract. *N,N'*-Di-*tert*-butyl-1,4-benzoquinone diimine *N,N'*-dioxide, C₁₄H₂₂N₂O₂, *M_r* = 250.34, monoclinic, *P*2₁/*c*, *a* = 10.5832 (8), *b* = 11.8392 (10), *c* = 11.6698 (7) Å, β = 96.714 (6)°, *V* = 1452.2 (2) Å³, *Z* = 4, *D_x* = 1.145 g cm⁻³, λ(Mo Kα, graphite monochromated) = 0.71069 Å, μ = 0.718 cm⁻¹, *F*(000) = 544, room temperature, *R* = 0.046 for 1440 observed reflections. The molecules lie on an inversion centre, with the independent unit formed by two different half molecules. The N atoms show an *sp*² hybridization so that, apart from the *tert*-butyl group, the molecule is planar. The pattern of bond lengths, in particular the ring deformation, suggests an important contribution of the quinone diimine limiting form to the possible resonating structures.

Introduction. The reaction of 1,4-dinitrobenzene (DNB) with alkyl Grignard reagents leads predomi-

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nantly to ring alkylated products from conjugate addition to the nitro group (Bartoli, Dalpozzo & Grossi, 1989). However, when DNB was reacted with *tert*-butylmagnesium chloride only traces of the alkylated product were found (Dalpozzo, Grossi & Ganazzoli, 1991). Upon quenching with saturated ammonium chloride solution the only characterizable product was the title compound *N,N'*-di-*tert*-butyl-1,4-benzoquinone diimine *N,N'*-dioxide, recovered in low yields. On the other hand, ESR analysis revealed at least three radical species (Lemaire, Marechal, Ramasseul & Rassat, 1965; Barbarella & Rassat, 1969; Dalpozzo *et al.*, 1991). Upon reduction with lithium aluminium hydride and palladium on charcoal, *N*-(4-*tert*-butylphenyl)-*N*-*tert*-butylhydroxylamine and the title compound could be isolated in comparable good yields. While the former compound was recognized as the parent of one of the radical species observed, the latter cannot account for any of them, although it might exist in a diamagnetic quinonic form or in a dinitroxide form. To

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Table 1. Final fractional coordinates and equivalent isotropic thermal factors, B_{eq} (Å²), with *e.s.d.*'s

B_{eq} is defined as one third of the trace of the orthogonalized B_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Molecule A				
O(1)	-0.1430 (2)	0.0885 (3)	0.2253 (2)	7.4 (2)
N(1)	-0.0309 (2)	0.0927 (2)	0.2799 (2)	3.7 (1)
C(1)	-0.0114 (3)	0.0489 (3)	0.3881 (2)	2.9 (1)
C(2)	-0.1057 (3)	0.0520 (3)	0.4611 (3)	3.3 (1)
C(3)	-0.1155 (3)	-0.0050 (3)	0.4329 (3)	3.4 (1)
C(4)	0.0696 (3)	0.1465 (3)	0.2144 (3)	3.9 (1)
C(5)	0.1142 (4)	0.2559 (4)	0.2732 (4)	6.2 (2)
C(6)	0.1776 (4)	0.0641 (4)	0.2067 (4)	7.0 (2)
C(7)	0.0076 (4)	0.1743 (4)	0.0935 (3)	6.3 (2)
Molecule B				
O(1)	0.3412 (2)	0.2615 (2)	0.0274 (2)	5.0 (1)
N(1)	0.4493 (2)	0.2197 (2)	0.0654 (2)	3.1 (1)
C(1)	0.4777 (3)	0.1117 (2)	0.0357 (2)	2.7 (1)
C(2)	0.5950 (3)	0.0565 (3)	0.0709 (2)	3.0 (1)
C(3)	0.3840 (3)	0.0509 (3)	-0.0368 (2)	3.0 (1)
C(4)	0.5383 (3)	0.2971 (3)	0.1425 (3)	3.3 (1)
C(5)	0.6578 (3)	0.3184 (3)	0.0848 (3)	4.7 (2)
C(6)	0.5658 (4)	0.2444 (3)	0.2630 (3)	4.8 (2)
C(7)	0.4692 (4)	0.4081 (3)	0.1540 (3)	5.0 (2)

Table 2. Bond lengths (Å) and angles (°) for the two independent half molecules

	Molecule A	Molecule B
O(1)—N(1)	1.281 (3)	1.277 (3)
N(1)—C(1)	1.358 (4)	1.368 (4)
N(1)—C(4)	1.519 (4)	1.529 (4)
C(1)—C(2)	1.420 (4)	1.421 (4)
C(1)—C(3)	1.424 (4)	1.421 (4)
C(2)—C(3')	1.349 (4) ⁱ	1.359 (4) ⁱⁱ
C(4)—C(5)	1.516 (6)	1.522 (5)
C(4)—C(6)	1.514 (6)	1.535 (4)
C(4)—C(7)	1.521 (5)	1.518 (5)
O(1)—N(1)—C(4)	115.3 (2)	116.0 (2)
O(1)—N(1)—C(1)	118.6 (3)	119.2 (2)
C(1)—N(1)—C(4)	126.1 (2)	124.8 (2)
N(1)—C(1)—C(3)	118.2 (3)	117.8 (3)
N(1)—C(1)—C(2)	125.1 (3)	124.5 (3)
C(2)—C(1)—C(3)	116.7 (3)	117.7 (3)
C(1)—C(2)—C(3')	120.5 (3) ⁱ	120.8 (3) ⁱⁱ
C(1)—C(3)—C(2)	122.8 (3) ⁱ	121.5 (3) ⁱⁱ
N(1)—C(4)—C(7)	107.9 (3)	109.5 (3)
N(1)—C(4)—C(6)	109.7 (3)	109.0 (2)
N(1)—C(4)—C(5)	109.2 (3)	107.5 (3)
C(6)—C(4)—C(7)	109.4 (3)	113.2 (3)
C(5)—C(4)—C(7)	108.2 (3)	108.2 (3)
C(5)—C(4)—C(6)	112.3 (3)	109.2 (3)

Symmetry operations for the primed atoms: (i) $-x, -y, 1-z$; (ii) $1-x, -y, -z$.

confirm the quinonic character of the title compound, a single-crystal X-ray analysis was carried out.

Experimental. Orange, prismatic crystals obtained by slow evaporation of a dichloromethane solution; crystal dimensions 0.25 × 0.30 × 0.30 mm, mounted on a glass fiber in a general orientation on a CAD-4 diffractometer. Cell constants from a least-squares fit of 2θ values of 25 reflections with 10 ≤ θ ≤ 19°, space group from systematic absences; data collection with θ/2θ scan mode; angular range 2.2 ≤ θ ≤ 25.0°; max. values of indices ±12, +14, +13; max. scan speed 6° min⁻¹; scan width (0.8 + 0.35tanθ)°; max. counting time 70 s; total background time 0.5 × scan time; 2538 independent data collected, 1440 used in refinement [$I \geq 3\sigma(I)$]. Three standard reflections (336, 336, 336) measured every hour for intensity and three (273, 336, 144) every 300 for orientation: no significant variation detected; data corrected for Lp factors; no absorption correction applied as judged from azimuthal ψ scans of reflections 352 and 463.

Structure solved by combination of direct methods with MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and Fourier techniques with SHELX76 (Sheldrick, 1976); refinement by full-matrix least squares with SHELX76 (Sheldrick, 1976) using anisotropic thermal factors for all non-H atoms. The asymmetric unit is formed by two independent half molecules, the other halves being related to the original ones by inversion centres at 0,0,½ (molecule A) and ½,0,0 (molecule B). Function minimized $\sum w(|F_o| - |F_c|)^2$

with weights $w = [\sigma^2(F_o) + g|F_o|^2]^{-1}$; refined value $g = 1.330 \times 10^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) with correction for real and imaginary parts of atomic dispersion. H atoms located on a difference Fourier map and held fixed in the last stages of refinement with isotropic collective thermal factors separately optimized for aromatic and alkyl hydrogens [final values $B = 4.3$ (4) and 8.3 (3) Å², respectively]. $R = 0.046$, $wR = 0.052$, $S = 1.05$ for 165 optimized parameters; largest $|\Delta/\sigma| = 0.03$; largest $\Delta\rho$ peak 0.16 e Å⁻³. Geometrical calculations with PARST (Nardelli, 1983). Final coordinates and equivalent isotropic thermal factors in Table 1, bond lengths and angles in Table 2.*

Discussion. A perspective view of the compound is shown in Fig. 1. Due to the close similarities between the two independent half molecules, we will only discuss average values unless otherwise specified.

The molecule is planar (aside from the *tert*-butyl groups), the largest deviations from the least-squares plane through atoms O(1), N(1), C(1) to C(4) being ±0.042 (4) Å in molecule A and ±0.007 (3) Å in molecule B. The least-squares planes through atoms O(1), N(1), C(1), C(4) and atoms N(1), C(1), C(2),

* List of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53914 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(3) form dihedral angles of $3.6(2)^\circ$ in molecule *A* and $0.5(1)^\circ$ in molecule *B*; this is the only significant conformational difference between the two molecules. The bond angles at N(1) (see Table 2) indicate an sp^2 hybridization, thus suggesting the presence of an extensive π conjugation. In fact, the average N—O distance, $1.279(3)$ Å, is quite similar to that found in azo dioxide derivatives, or nitroso dimers [see, e.g., *cis*-azobenzene dioxide (Dieterich, Paul & Curtin, 1974), with an average of $1.264(4)$ Å or *trans*-2,2'-dicarboxyazobenzene dioxide (Dieterich *et al.*, 1974) with $1.267(3)$ Å], or in *p*-azoxy anisole [$1.279(4)$ Å (Krigbaum, Chatani & Barber, 1970)]. It is also equal to those found in *p*-methoxyindophenol *N*-oxide, $1.266(4)$ Å (Romers & Hesper, 1966) and in paramagnetic nitroxides: for example, 2,2,5,5-tetramethyl-3-*X*-1-pyrrolidinyloxy derivatives have an N—O separation of $1.272(3)$ Å for $X = \text{COOH}$ (Ament, Wetherington, Moncrief, Flohr, Mochizuki & Kaiser, 1973; Wetherington, Ament & Moncrief, 1974) and $1.272(5)$ Å for $X = \text{NOH}$ (Chion & Thomas, 1975).

The C(1)—N(1) bond length, $1.363(4)$ Å, is quite short and compares well with those found in *p*-methoxyindophenol *N*-oxide [$1.357(5)$ Å (Romers & Hesper, 1966)] and in conjugated push-pull ethylenes such as 1,1-bis(dimethylamino)-2-nitroethylene ($1.34\text{--}1.37$ Å; Ganazzoli, Meille & Gronchi, 1986). The C—C distances in the six-membered ring belong to two significantly distinct sets (see Table 2): the first set comprises the C(1)—C(2) and C(1)—C(3) distances (average 1.422 Å), the second set the much shorter C(2)—C(3') distances (average 1.354 Å). These bond lengths are strongly suggestive of a partial quinonoid character of the molecule, much larger indeed than that claimed, e.g., for *p*-nitroaniline derivatives (Colapietro, Domenicano, Marcianti & Portalone, 1982; Hughes & Trotter, 1971) though of course not as large as *p*-benzoquinone itself, where the corresponding values are $1.467(6)$ and $1.312(8)$ Å, respectively (Trotter, 1960). The evidence points to an electronic structure which may be largely described by the quinonic form, the 'nitroxide' form being less important. On

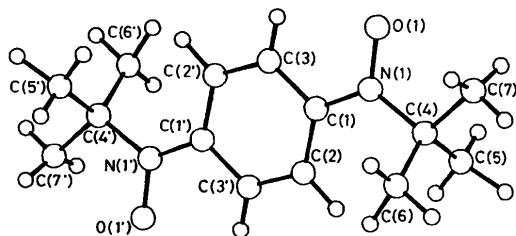
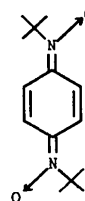


Fig. 1. A perspective view of one molecule with the atom-labelling scheme. The primed atoms are related to the unprimed ones by an inversion centre located at the centre of the ring. H atoms have not been labelled for clarity.

the other hand, a better description of the electronic structure may be given in terms of π orbitals delocalized over the whole molecule (apart from the *tert*-butyl moiety) with no unpaired electrons, in agreement with the diamagnetism of the compound (Dalpozzo, Grossi & Ganazzoli, 1991).



Angular deformations in the six-membered ring are consistent with those found in *p*-benzoquinone (Trotter, 1960) and the opening of the C(1)—N(1)—C(4) angle is due to the steric repulsion between the *tert*-butyl group and C(2) [C(2)⋯C(6) $3.176(5)$ Å and H(2)⋯H(6A) 2.06 Å].

No unusual intermolecular contacts are present and the independent molecules are arranged in the crystal with main planes forming an angle of about 85° .

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