Unconventional Reaction of Diazomethane with 1,3,6-Trihydroxy-2-methyl-4-nitrobenzene; *X*-Ray Crystal Structure of (*E*)-3,6-Dihydroxy-2-methyl-1,4-benzoquinone 4-Methoxyimine *N*-Oxide

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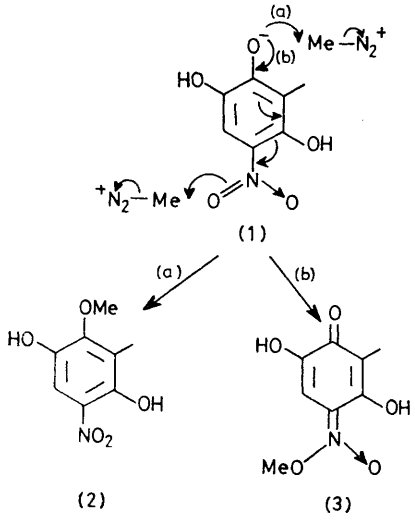
Summary Treatment of 1,3,6-trihydroxy-2-methyl-4-nitrobenzene (protonated **1**) with diazomethane produces not only the expected 1-methoxy derivative but also a substantial amount of an isomer with the novel structure (*E*)-3,6-dihydroxy-2-methyl-1,4-benzoquinone 4-methoxyimine *N*-oxide (**3**); the structure of (**3**) is confirmed by *X*-ray analysis.

DURING synthetic studies on the mitomycin antibiotics the selective monomethylation of 1,3,6-trihydroxy-2-methyl-4-nitrobenzene (protonated **1**) with diazomethane was investigated. It was anticipated that the most acidic 1-hydroxy group would be preferentially attacked and indeed the expected 1-methoxy derivative (**2**) was obtained as yellow needles, m.p. 137—139 °C [τ (CF_3CO_2H) 2·33 (1H, s, =CH–), 5·96 (3H, s, –OMe), 7·65 (3H, s, –C–Me)]. However, an equal quantity of a less-soluble, deep red, thermolabile isomer was also produced; this could be crystallised rapidly from acetonitrile to give prisms which decomposed vigorously at 146 °C [τ (CF_3CO_2H) 2·55 (1H, s, =CH–), 5·57 (3H, s, –OMe), 7·70 (3H, s, –C–Me)]. These and other spectroscopic properties suggested the novel structure (*E*)-3,6-dihydroxy-2-methyl-1,4-benzoquinone 4-methoxyimine *N*-oxide (**3**) for the unexpected product. The formation of (**2**) and (**3**) may be rationalised by the two modes of interaction of the diazomethane conjugate acid with the phenolate ion (**1**) as shown in the Scheme. The postulated structure for (**3**) was subsequently verified by *X*-ray crystal analysis.



SCHEME

Crystal data: $C_8H_9NO_5$, *M* 199·17, triclinic, $P\bar{1}$, *a* = 4·470(4), *b* = 9·733(6), *c* = 10·526(6) Å, α = 103·88(5), β = 100·20(5), γ = 95·84(5)°, *U* = 432·5(5) Å^3, D_m = 1·529 g cm^{-3}, *Z* = 2, μ = 0·7 cm^{-1} (Mo-K_α). The unit cell was measured and intensities ($0 < 2\theta < 65°$) collected using a diffractometer with monochromated Mo-K_α radiation, and a crystal 0·55 × 0·25 × 0·1 mm.

The structure was solved with difficulty; multisolution Σ_2 sign expansion using the program SHEL-X gave no sensible *E*-maps. The program XCSD gave *E*-maps which showed a 'chicken-wire' effect of multiple 6-membered rings. A fragment of 13 peaks was chosen as a starting point for difference syntheses; however, no progress could be made in $P\bar{1}$. The space-group was changed to *P*1, when iterative difference syntheses revealed all but 3 of the atoms of two

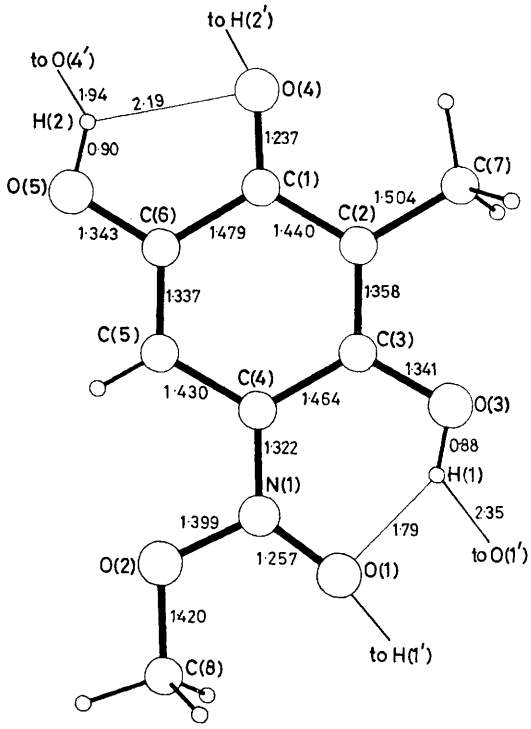


FIGURE. A perspective view of (**3**), showing bond lengths (Å) and the bifurcated hydrogen bonding. E.s.d.s in bond lengths: ± 0·03 Å (bonds involving H atoms) and ± 0·004 Å (all other bonds). Primes indicate symmetry related atoms.

molecules related by a centre of symmetry; several peaks of the initial 13 turned out to be false. Least-squares refinement, followed by a difference synthesis, gave all the missing atoms. The space-group was changed back to $P\bar{1}$, and least-squares refinement (all non-hydrogen atoms anisotropic)

proceeded to a conventional R of 4·9% for 1333 unique reflexions with $F > 4\sigma(F)$.†

A diagram of the molecule is given in the Figure. The bond lengths establish the ring as the quinonoid structure (**3**) which contains bifurcated hydrogen bonds. The two intermolecular bonds link the structure in infinite parallel sheets.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.