Resonance effects in substituted benzoquinones. Crystal and molecular structure of 2,5-bisazetidino-1,4-benzoquinone monohydrate and 2,5-bishexamethylenimino-1,4-benzoquinone

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Crystal data for the title quinones are: $C_{12}H_{14}N_2O_2 \cdot H_2O$ (4), monoclinic, with $a = 5,017(3)$, $b = 9,793(5)$, $c = 12,789(6)$ Å, $\beta = 95,76(2)°$, $Z = 2$, space group $P2_1/n$; $C_{18}H_{26}N_2O_2$ (7), triclinic, with $a = 13,193(7)$, $b = 6,871(3)$, $c = 9,261(5)$ Å, $\alpha = 98,03(2)$, $\beta = 102,12(2)$, $\gamma = 94,11(2)°$, $Z = 2$, space group $P\bar{1}$. These and other similar compounds exhibit varying contributions from the quadrupolar form (II). Correlations between structural and ¹H n.m.r. data are discussed.

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Kristallografiese gegewens vir die twee kinone is: $C_{12}H_{14}N_2O_2 \cdot H_2O$ (4), monoklinies, met $a = 5,017(3)$, $b = 9,793(5)$, $c = 12,789(6)$ Å, $\beta = 95,76(2)°$, $Z = 2$, ruimtegroep $P2_1/n$; $C_{18}H_{26}N_2O_2$ (7), triklinies, met $a = 13,193(7)$, $b = 6,871(3)$, $c = 9,261(5)$ Å, $\alpha = 98,03(2)$, $\beta = 102,12(2)$, $\gamma = 94,11(2)°$, $Z = 2$, ruimtegroep $P\bar{1}$. Hierdie en soortgelyke verbindings vertoon verskillende bydraes van die kwadrupolêre vorm (II). Vergelykings tussen strukturele en ¹H-k.m.r.-gegewens word bespreek.

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It has been proposed that 2,5-bisaminated 1,4-benzoquinones can exist as resonance hybrids of two canonical forms (I) and (II). The relative contribution of the quadrupolar form (II) depends on the nature of the substituents at the 2- and 5-positions, and has been measured in solution using both ¹H n.m.r. spectroscopy and polarography.[1,2] The spectroscopic method indicated that the importance of the contribution of the quadrupolar form (II) decreased in the series in the order $4 > 5 > 7 > 6 > 3$. Measurements of half-wave potentials were essentially in agreement but reversed the order of 4 and 5. Corresponding data for a series of 2-aminated-1,4-naphthoquinones revealed similar trends.[3]

It would be expected that the relative contribution of (I) and (II) to the structure would be revealed from the changes in bond lengths as the substituents are changed in the sequence 3—7. A crystallographic study of the benzoquinones (3), (5), and (6) revealed agreement with the spectroscopic and polarographic results.[4] In order to complete the series, we now report the structures of 2,5-bisazetidino-1,4-benzoquinone (4) and 2,5-bishexamethylenimino-1,4-benzoquinone (7).
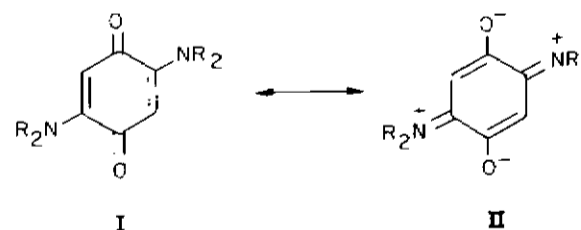
3	NR_2 =	aziridino
4	NR_2 =	azetidino
5	NR_2 =	pyrrolidino
6	NR_2 =	piperidino
7	NR_2 =	hexamethylenimino

Experimental

The azetidino-compound (4) was prepared as described by Marxer,[5] and the hexamethylenimino-compound (7) as described by Cameron et al.[3] Both compounds crystallize as bright-red needles elongated along b. Preliminary cell dimensions and space groups were determined photographically. Accurate cell parameters were then obtained by least squares from the settings of 25 reflections measured on a four-circle diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0,7107$ Å). During data collection, three reference reflections were

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Table 1 Crystal data and experimental and refinement parameters for the crystal structures of **4** and **7**

	4	**7**
Crystal data		
Molecular formula	$C_{12}H_{14}N_2O_2 \cdot H_2O$	$C_{18}H_{26}N_2O_2$
Mr	218	302
Space group	$P2_1/n$	$P\bar{1}$
a/Å	5,017(3)	13,193(7)
b/Å	9,793(5)	6,871(3)
c/Å	12,789(6)	9,261(5)
$a/°$	—	98.03(2)
$\beta/°$	95,76(2)	102,13(2)
$\gamma/°$	—	94,11(2)
$U/Å^3$	625,17	808,29
D_c/Mg m^{-3}, for $Z = 2$	1,15	1,24
μ(Mo–$K\alpha$)/cm^{-1}	0,63	0,46
F(000)	272	326
Data collection		
Crystal dimensions/mm	0,50 × 0,15 × 0,15	0,35 × 0,25 × 0,17
Scan width/$°\theta$	1,2	1,2
Scan speed/$°\theta$s^{-1}	0,03	0,04
Range of reflections	$3° < \theta < 23°$	$3° < \theta < 23°$
Number of unique reflections	934	2259
Observed reflection criteria	$I(\text{rel}) > 2\sigma I(\text{rel})$	$I(\text{rel}) > 2\sigma I(\text{rel})$
Number of reflections observed	852	2217
Final refinement		
Number of variables	100	215
$R = \Sigma\|\ \|Fo\| - \|Fc\|\ \|/\Sigma\|Fo\|$	0,044	0.044
$R_w = \Sigma w^{1/2}\|\ \|Fo\| - \|Fc\|\ \|/\Sigma w^{1/2}\|Fo\|$ where $w = (\sigma^2 F)^{-1}$	0,054	0.040
U for quinonoid hydrogens	0,04(1)	0,04(1); 0,05(1)[a]
U for methylene hydrogens	0,06(0)	0.07(0); 0,08(0)[a]

[a] Values refer to molecules A and B respectively.

periodically monitored to check crystal stability. Crystal data and experimental details are listed in Table 1. The data were corrected for Lorentz-polarization effects but not for absorption.

Solution and refinement of the structures

The azetidino-compound (4) was solved by the automatic centrosymmetric routine of the SHELX program system,[6] in which an E map yielded the positions of all the heavy atoms in the organic moiety. Subsequent least-squares refinement followed by difference Fourier maps revealed the positions of most hydrogen atoms and the oxygen atom of a water of crystallization (W). Further refinement yielded the position of one water-hydrogen atom unequivocally, while the second gave rise to a diffuse electron-density peak located at inversion centres $\frac{1}{2},\frac{1}{2},0$ and $0,\frac{1}{2},0$ (Figure 1).

The final refinement was carried out with the heavy atoms treated anisotropically and with the quinonoid and methylene hydrogens constrained at 1.08 Å from their respective carbon atoms, their positions being dictated by the geometry of the molecule. The isotropic temperature factors of the methylene protons were refined as a single parameter.

Regarding the refinement of the water hydrogen, we recognized that the W·····W distance of 2.81 Å was too long for a symmetrical hydrogen bond,[7] and we considered HW(2) as disordered and constrained at 1,0 Å from W. We refined it as two half-atoms with a fixed temperature factor. The other water-hydrogen atom, HW(1), was similarly constrained at 1,0 Å from W, and is hydrogen-bonded to the quinone O(1), as shown in Figure 1. The hydrogen-bonding scheme is detailed in Table 3c.
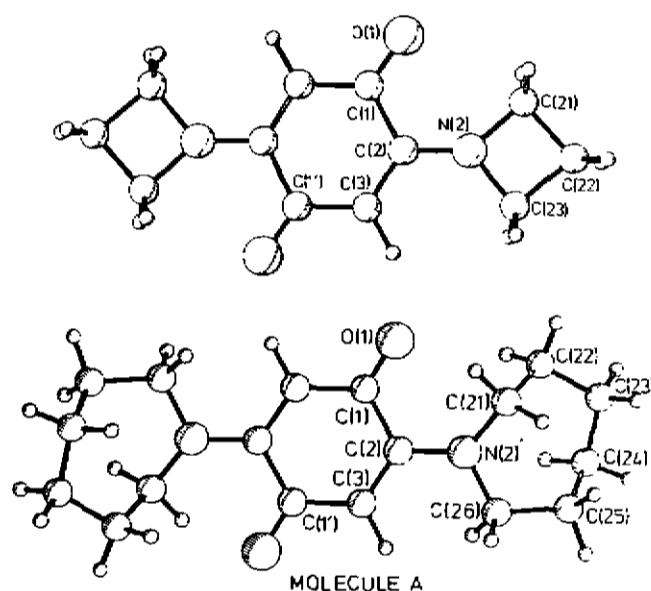
The hexamethylenimino-compound (7) was solved and refined in a similar manner. There are two centrosymmetric independent molecules, with the molecular centres at 0,0,0 and $0,0,\frac{1}{2}$. As checks for the correctness of the structures, difference Fourier maps were computed. These showed no peaks >0,07 electrons Å^{-3}. Details of the refinements are given in Table 1 and the final atomic coordinates of the heavy atoms in Table 2.
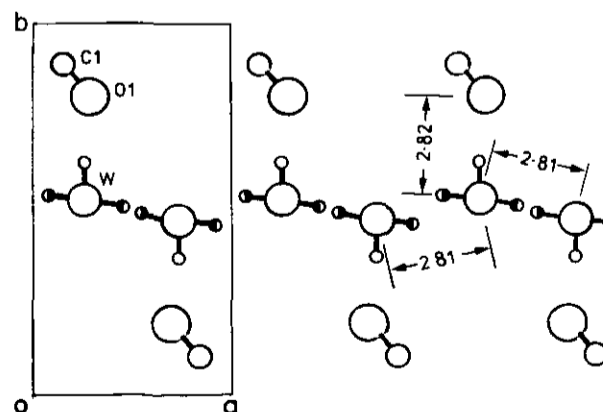
Figure 1 The hydrogen-bonding scheme. Disordered hydrogen atoms are shown as shaded circles.

Table 2 Fractional atomic coordinates ($\mathring{A} \times 10^4$) of the non-hydrogen atoms, with e.s.d.'s in parentheses

| | Azetidino-compound (4) | | | Hexamethylenimino-compound (7) | | | | | |
| | | | | Molecule A | | | Molecule B | | |
	x	y	z	x	y	z	x	y	z
C(1)	1506(5)	−1806(2)	549(2)	449(2)	1938(3)	721(3)	889(2)	−964(3)	5577(3)
O(1)	2919(4)	−1955(2)	1052(1)	895(1)	3615(2)	1242(2)	1708(1)	−1720(2)	5966(2)
C(2)	2144(5)	401(2)	735(2)	929(2)	136(3)	1203(3)	788(2)	1146(3)	6228(3)
N(2)	4171(4)	705(2)	1445(2)	1818(1)	369(3)	2295(2)	1558(1)	2151(3)	7348(2)
C(3)	686(5)	1407(3)	186(2)	483(2)	−1668(3)	423(3)	−62(2)	1997(3)	5574(3)
C(21)	5995(5)	−49(3)	2221(2)	2103(2)	2080(3)	3507(3)	2259(2)	1202(4)	8430(3)
C(22)	7181(5)	1322(3)	2606(2)	3007(2)	3489(4)	3353(3)	3359(2)	1200(4)	8171(3)
C(23)	5201(5)	2050(3)	1797(2)	4074(2)	2737(4)	3745(3)	4022(2)	3199(4)	8686(3)
W	2613(5)	−4724(2)	448(2)						
C(24)				4148(2)	676(4)	2939(3)	3519(2)	4931(2)	8078(3)
C(25)				3489(2)	−963(4)	3375(3)	2545(2)	5392(4)	8654(3)
C(26)				2371(2)	−1390(3)	2491(3)	1529(2)	4301(2)	7708(3)

Figure 2 Perspective views of the compounds (4) and (7) (molecule A).

Table 3a Principal bond lengths (Å) with e.s.d.'s in parentheses

| | Azetidino-compound (4) | Hexamethylenimino-compound (7) | |
		Molecule A	Molecule B
C(1)-O(1)	1,245(3)	1,239(3)	1,240(3)
C(1)-C(2)	1,505(3)	1,511(3)	1,516(3)
C(2)-C(3)	1,377(3)	1,368(3)	1,370(3)
C(3)-C(1')	1,408(2)	1,426(2)	1,421(2)
C(2)-N(2)	1,327(3)	1,361(3)	1,357(3)
N(2)-C(21)	1,479(3)	1,474(3)	1,471(3)
C(21)-C(22)	1,530(4)	1,524(3)	1,520(3)
C(22)-C(23)	1,535(4)	1,524(3)	1,533(3)
N(2)-C(23)	1,468(3)		
N(2)-C(26)		1,469(3)	1,473(3)
C(23)-C(24)		1,526(4)	1,523(3)
C(24)-C(25)		1,523(4)	1,528(4)
C(25)-C(26)		1,516(3)	1,519(3)

Table 3b Bond angles (°) with e.s.d.'s in parentheses

| | Azetidino-compound (4) | Hexamethylenimino-compound (7) | |
		Molecule A	Molecule B
C(2)-C(1)-O(1)	118,6(2)	120,4(2)	120,5(2)
N(2)-C(2)-C(1)	117,5(2)	119,5(2)	119,9(2)
C(3)-C(2)-C(1)	121,2(2)	117,3(2)	117,2(2)
C(3)-C(2)-N(2)	121,3(2)	123,0(2)	122,7(2)
C(2)-C(3)-C(1')	121,3(2)	123,7(2)	123,7(2)
C(2)-C(1)-C(3')	117,4(2)	118,8(2)	118,7(2)
O(1)-C(1)-C(3')	118,6(2)	120,6(2)	120,6(2)
C(23)-N(2)-C(2)	129,3(2)		
C(21)-N(2)-C(23)	93,9(2)		
C(22)-C(23)-N(2)	88,5(2)		
C(22)-C(21)-N(2)	88,4(2)	113,7(2)	113,5(2)
C(21)-N(2)-C(2)	136,6(2)	123,7(2)	123,9(2)
C(21)-C(22)-C(23)	89,2(2)	114,5(2)	114,2(2)
C(2)-N(2)-C(26)		116,9(2)	117,2(2)
C(21)-N(2)-C(26)		117,4(2)	117,4(2)
C(22)-C(23)-C(24)		114,8(2)	114,7(2)
C(23)-C(24)-C(25)		114,0(2)	113,1(2)
N(2)-C(26)-C(25)		114,8(2)	113,9(2)
C(24)-C(25)-C(26)		115,9(2)	115,2(2)

Table 3c Hydrogen-bonding data with e.s.d.'s in parentheses (refer to Figure 1)

Bond[a]	Length/Å
W^i .... O(1)^i	2,82(1)
W^i .... W^ii	2,81(1)
W^i .... W^iii	2,81(1)

[a] Symmetry code: (i) $x, 1+y, z$; (ii) $1+x, y, -z$; (iii) $2+x, y, -z$

Discussion

The principal bond lengths and angles are given in Tables 3a and 3b respectively. Perspective views of both compounds are given in Figure 2.

In both structures the molecular centres coincide with crystallographic centres of inversion. The azetidino-quinone

(4) is planar with all atoms lying within 0,15(5) Å of the least-squares plane calculated through the atoms C(1), C(2), C(3), C(1'), C(2'), and C(3'). The hexamethylenimino-quinone (7) has two independent molecules, A and B, which have similar conformations, and essentially planar quinonoid rings. The internal torsion angles of the hexamethylenimino-rings of 7 are shown in Figure 3. They closely approximate the energetically favourable twist-chair form of cycloheptanes.[8]
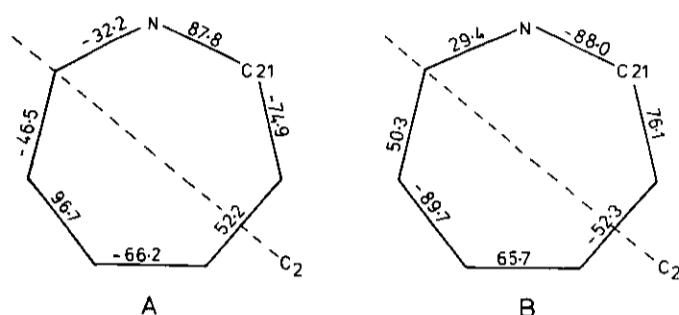

Figure 3 Internal torsion angles for the seven-membered rings of the hexamethylenimino-compound (7).

We have calculated asymmetry parameters for the seven-membered rings, using the formula[9]

$$\Delta C_2 = \sqrt{\sum_{i=1}^{3} (\varphi - \varphi_i^1)^2}$$

and have found values of $\Delta C_2^{(2,3)} = 11,0°$ and $\Delta C_2^{(2,3)} = 13,6°$ for molecules A and B respectively.

The four bonds in the conjugated system, N(2)—C(2)—C(3)—C(1')—O(1'), are compared with the lengths obtained for compounds (3), (5), and (6), and are shown in Table 4. These bonds alternatively increase or decrease in length down the series (4)-, (5)-, (7)-, (6)-, (3)-1,4-benzoquinone. The changes in bond lengths illustrate the degree of delocalization of the nitrogen lone pair and hence the relative contributions of (I) and (II) to the structures.

The N(2)—C(2) bond length is a measure of the degree of

lone-pair participation in the conjugated system. It has been proposed that 2,5-bisaminated-1,4-benzoquinones can be considered as coupling products of two trimethine-merocyanine structural elements,[12] resulting in the equalization of bonds C(2)—C(3) and C(3)—C(1') as the degree of delocalization increases. A plot of the bond length against the ratio of the C(2)—C(3) and C(3)—C(1') bond lengths is shown in Figure 4. The curves shown in Figure 4 reveal that the equalization of bond lengths increases with increasing electron donating power of the substituents, in the order 4>5>7>6>3. This is the same sequence as obtained from [1]H n.m.r. and, partially, from polarographic data.

The chemical shift of the quinonoid proton is an effective measure of the electron density in the conjugated system and the concomitant partial charges on the oxygen and nitrogen atoms, i.e. of the contribution of the quadrupolar resonance form (II). The correlation between the bond ratio $d[C(2)—C(3)]/d[C(3)—C(1')]$ and the chemical shift is shown in Figure 4.

Here again, the increasing bond equalization is accompanied by an increase in the chemical shift of the
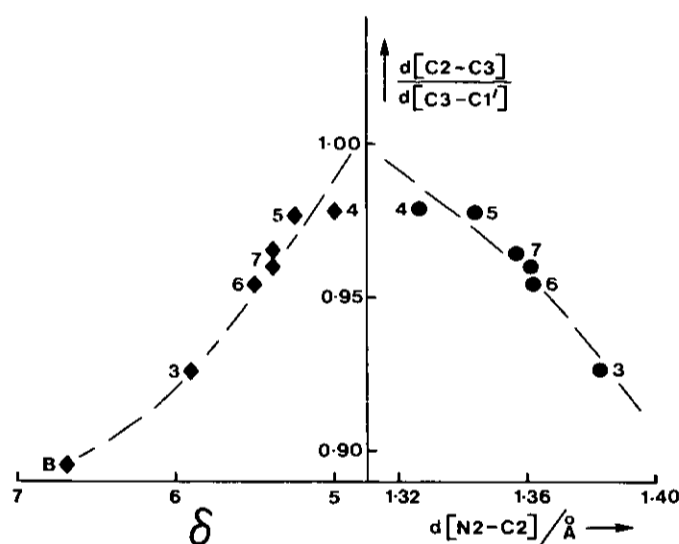

Figure 4 A plot of the ratio of the [C(2)—C(3)]/[C(3)—C(1')] bond lengths against the N(2)—C(2) bond length and the chemical shift of the quinonoid proton.

Table 4 Comparison of selected bond lengths (Å) and related parameters in 2,5-bisaminated-1,4-benzoquinones

NR$_2$	Bond lengths					Distance[a] Å	Sum of angles[b] °
	N(2)—C(2)	C(2)—C(3)	C(3)—C(1')	C(1')—O(1')	C(2)—C(1)		
Azetidino (4)	1,327(3)	1,377(3)	1,408(2)	1,245(3)	1,505(3)	0,04	359,8
Pyrrolidino (5)[c]	1,344(5)	1,374(5)	1,407(5)	1,245(5)	1,520(5)	0,02	359,9
Hexamethylenimino (7)[d] A	1,361(3)	1,368(3)	1,426(2)	1,239(3)	1,511(3)	0,15	358,0
B	1,357(3)	1,370(3)	1,421(2)	1,240(3)	1,516(3)	0,10	358,5
Piperidino (6)[c]	1,362(3)	1,366(4)	1,431(4)	1,237(3)	1,517(4)	0,18	355,4
Aziridino (3)[c]	1,383(4)	1,347(4)	1,455(5)	1,244(3)	1,516(4)	0,59	302,8
Benzoquinone[f]	—	1,322(8)	1,477(6)	1,222(8)	1,477(6)	—	—

[a] Distance of N from the plane defined by the three atoms bonded to it.
[b] Sum of angles about N.
[c] Ref. 4.
[d] Values for molecules A and B.
[e] Ref. 10.
[f] Values for 1,4-benzoquinone (ref. 11).

quinonoid proton, as the resonance contributor (II) plays a greater role in the series $3<6<7<5<4$.

The hybridization about the nitrogen atom is of interest as this is also indicative of the degree of lone-pair participation in the conjugated system. The distance of the nitrogen atom from the plane defined by the three atoms bonded to it, and the sum of the angles about N, are a measure of the sp^2 character of the nitrogen atom. These parameters are listed in the last two columns of Table 4.

The distance of the nitrogen atom from the plane defined by the three atoms bonded to it increases in the order $4\approx5<7<6<3$. This is indicative of decreasing sp^2 character of the nitrogen atom down the series. The sum of the angles for an ideally sp^2 hybridized nitrogen atom is approximately 360°. The sum also decreases in the order $4\approx5>7>6>3$. In the case of compound (3) the sum of the angles is reduced owing to the small internal angle of the three-membered ring.

The C(1)–C(2) bond, which is not part of the conjugated system, is longer than that found in 1,4-benzoquinone in all the compounds listed in Table 4. This is in agreement with the bond lengths determined for similar compounds.[12] The C(1)–C(2) bond is the coupling bond for the two trimethine–merocyanine structural elements, and the lengthening of this bond with respect to the parent 1,4-benzoquinone has been predicted from quantum-mechanical calculations.[13] This observed lengthening on 2,5-disubstituted 1,4-benzoquinone is therefore further evidence for the concept that the 2,5-bisaminated-1,4-benzoquinones may be considered to be coupling products of two dipolar trimethine–merocyanine structural units.

All calculations were carried out on a UNIVAC 1108 computer system at the University of Cape Town.

Supplementary material

Tables of hydrogen atomic coordinates, anisotropic thermal parameters, and structure factors are available upon request from the photocopying section, CSIR Library Division, CSTI, P.O. Box 395, Pretoria 0001.

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