Comparison of the crystallographically determined resonance hybrids of 2,5-bispyrrolidino- and 2,5-bispiperidino 1,4-benzoquinones

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The crystal structures of the two title compounds have been determined and compared. The crystallographic data correlate very well with an earlier contention that in solution the pyrrolidino-quinone (5) exhibits a greater contribution to its structure from the quadrupolar form (II) than does the piperidino-quinone (6). Both compounds crystallize in the triclinic space group $P\bar{1}$ and have one centrosymmetric molecule per unit cell. The pyrrolidino-quinone unit cell dimensions are $a = 4,925(3)$, $b = 6,533(4)$, $c - 10,002(5)$ Å, $\alpha = 90,8(2)$, $\beta = 104,3(2)$, and $\gamma = 93,8(2)°$, and those for the piperidino-quinone are $a = 8,437(5)$, $b = 6,658(4)$, $c - 6,839(4)$ Å, $\alpha = 99,6(2)$, $\beta = 108,4(2)$, and $\gamma = 86,7(2)°$.

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Die kristalstrukture van die twee titelverbindings is bepaal en vergelyk. Die kristallografiese gegewens bevestig 'n vroeëre bewering dat die pirrolidinokinoon (5), in oplossing, 'n groter struktuurbydrae van die kwadrapolêre vorm (II) as die piperidinokinoon (6) vertoon. Albei verbindings kristalliseer in die trikliniese ruimtegroep $P\bar{1}$ met een sentrosimmetriese molekuul per eenheidsel. Die pirrolidinokinoon het selkonstantes $a = 4,925(3)$, $b - 6,533(4)$, $c = 10,002(5)$ Å, $\alpha = 90,8(2)$, $\beta = 104,3(2)$, $\gamma = 93,8(2)°$, en die piperidinokinoon het $a = 8,437(5)$, $b = 6,658(4)$, $c = 6,839(4)$ Å, $\alpha = 99,6(2)$, $\beta = 108,4(2)$, en $\gamma = 86,7(2)°$.

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In benzoquinones (3)—(7) bearing the homologous series of cyclic secondary amino-substituents, aziridino, azetidino, pyrrolidino, piperidino, and hexamethylenimino, the relative degree of delocalization involving the nitrogen lone pair and the quinonoid system, i.e. the relative contribution from the quadrupolar form (II), has been conveniently measured[5,6,7] in solution using both ^{1}H nuclear magnetic resonance spectroscopy and polarographic half-wave potential measurements. The spectroscopic method indicated that the importance of the contribution of the quadrupolar form (II) decreased in the series in the order $4 > 5 > 7 > 6 > 3$. Half-wave potential measurements were in qualitative agreement, except that the relative contribution of form (II) to 4 and 5 was reversed. Corresponding data[7] for a similar series of 2-aminated 1,4-naphthoquinones were in close accord with these results. Suggestions were put forward[7] to explain the observed differences on varying the amino-substituent.

We report here a comparison of the crystal structures of 2,5-bispyrrolidino-1,4-benzoquinone (5) and 2,5-bispiperidino-1,4-benzoquinone (6). The structure of 6, which has been reported previously,[8] was solved using photographically collected data and refined to an R of 0,096. Since this study requires accurate bond length determinations it was felt necessary to redetermine the structure using diffractometer data. Our results for the piperidino-compound (6) correspond very well with those previously published. We also include data for 2,5-bisaziridino-1,4-benzoquinone (3)[9] and 1,4-benzoquinone[10] for comparison purposes.
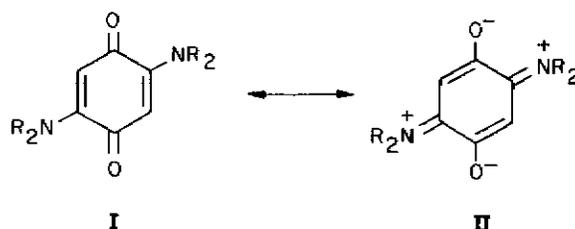
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	NR$_2$ =
3	aziridino
4	azetidino
5	pyrrolidino
6	piperidino
7	hexamethylenimino

Experimental

2,5-Bispyrrolidino-1,4-benzoquinone (5) and 2,5-bispiperidino-1,4-benzoquinone (6) were prepared as described by Marxer.[11] They were both recrystallized from ethanol. Red plates, m.p. 238—240 °C (decomp.), crystallized in the former case, and deep red crystals, m.p. 177—178 °C, in the latter.

Preliminary data were obtained from oscillation and Weissenberg photographs (Cu-$K\alpha$ radiation, $\lambda = 1,542$ Å) and indicated a triclinic space group in both cases. The cell parameters were obtained by least squares from the settings of 25 reflections measured on a Philips PW1100 four-circle diffractometer with Mo-$K\alpha$ radiation ($\lambda = 0,7107$ Å, graphite monochromated). The ω-2θ scan technique was used. The background was counted on both sides of the peak for half the peak scan time. The intensities of three standard reflections measured every hour remained constant to within 1,1 and 1,6% of their mean values for 5 and 6 respectively. Lorentz-polarization but no absorption corrections were applied. E-statistics were calculated as a function of sinθ for both sets of data and they indicated centrosymmetric structures, space groups $P\bar{1}$.

The pyrrolidino-compound (5) was solved by the automatic centrosymmetric routine of the SHELX program system.[12] The third E-map yielded all the non-hydrogen atoms. After three cycles of least squares refinement with the atoms treated isotropically, a difference map yielded all but one of the hydrogen atoms. In the final refinement all the non-hydrogen atoms were treated anisotropically. The quinonoid hydrogen and the methylene hydrogens were constrained at 1,08 Å from their respective C atoms, their positions being dictated by the geometry of the molecule. The isotropic temperature factors of the methylene hydrogens were refined as a single parameter.

The piperidino-compound (6) was solved using previously quoted atomic coordinates.[8] In the final refinement it was treated in the same manner as 5. Details of the refinements are given in Table 1. Final atomic coordinates for the non-hydrogen atoms are given in Table 2.

Lists of hydrogen atomic coordinates, anisotropic thermal parameters, and structure factors have been deposited as supplementary material (q.v.). Perspective views of both the pyrrolidino- (5) and piperidino- (6) compounds with atomic nomenclature are shown in Figure 1. Bond lengths and angles for 5 and 6, together with comparative data for the aziridino-compound (3), are given in Figure 2.
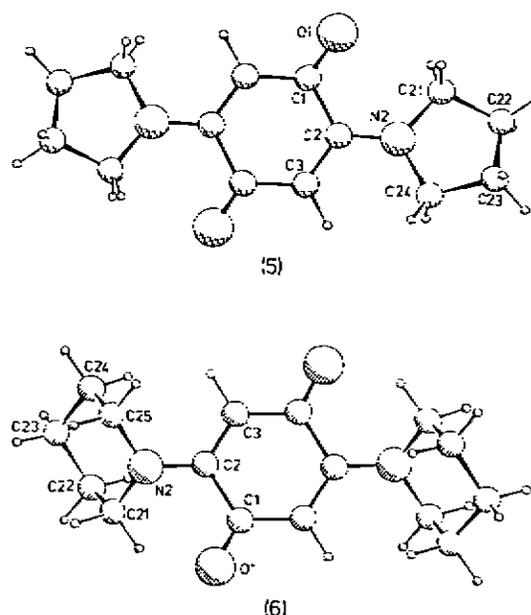

Fig. 1 Perspective views of 2,5-bispyrrolidino-1,4-benzoquinone (5) and 2,5-bispiperidino-1,4-benzoquinone (6).

Table 1 Crystal and intensity data and refinement parameters for the structures

	5	6
Crystal data		
Molecular formula	$C_{14}H_{18}N_2O_3$	$C_{16}H_{22}N_2O_2$
M.W.	246	274
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	4.925(3)	8,437(5)
b/Å	6.533(4)	6.658(4)
c/Å	10,002(5)	6.839(4)
α/°	90.8(2)	99,6(2)
β/°	104.3(2)	108,4(2)
γ/°	93,8(2)	86.7(2)
U/Å³	311,0	359,4
D_c for $Z = 1$/g cm⁻³	1,31	1,27
μ (Mo-$K\alpha$)/cm⁻¹	0,52	0,48
$F(000)$	132	148
Data collection		
Crystal dimensions/mm	0,20 × 0,18 × 0,05	0,20 × 0,18 × 0,18
Scan width/°θ	1,2	1,2
Scan speed/°θ s⁻¹	0,02	0,04
Range of reflections/°θ	$3 < \theta < 20$	$3 < \theta < 23$
Number of unique reflections	559	981
Observed reflection criteria	$I(rel.) > \sigma I(rel.)$	$I(rel.) > 2\sigma I(rel.)$
Number of reflections observed	411	687
Final refinement		
Number of variables	84	93
$R = \Sigma \mid \mid Fo \mid - \mid Fc \mid \mid /\Sigma \mid Fo \mid$	0,052	0,052
$R_w = \Sigma w^{\frac{1}{2}} \mid \mid Fo \mid - \mid Fc \mid \mid /\Sigma w^{\frac{1}{2}} \mid Fo \mid$ where $w = (\sigma^2 F)^{-1}$	0,044	0,043
U (for quinonoid hydrogens)/Å²	0,05(1)	0,06(1)
U (for methylene hydrogens)/Å²	0,14(1)	0.08(1)

Table 2 Fractional atomic coordinates (x10⁴) of the heavy atoms

	x/a	y/b	z/c
2,5-Bispyrrolidino-1,4-benzoquinone			
C(1)	436(11)	−963(7)	1307(5)
O(1)	788(8)	−1736(5)	2463(3)
C(2)	−1156(9)	963(7)	1025(5)
C(3)	−1463(10)	1816(7)	−246(5)
N(2)	−2136(8)	1822(6)	2025(4)
C(21)	−2206(11)	1017(7)	3401(5)
C(22)	−3987(13)	2473(8)	3949(5)
C(23)	−3815(14)	4410(8)	3228(5)
C(24)	−3489(11)	3785(7)	1796(5)
2,5-Bispiperidino-1,4-benzoquinone			
C(1)	−1117(4)	−1538(5)	−14(5)
O(1)	−2187(3)	−2836(3)	−273(4)
C(2)	−1389(4)	675(5)	798(4)
C(3)	−326(4)	2080(5)	664(5)
N(2)	−2748(3)	1168(4)	1454(4)
C(21)	−3375(4)	−99(5)	2626(5)
C(22)	−2721(4)	698(5)	4955(5)
C(23)	−3170(5)	2946(5)	5431(5)
C(24)	−2560(5)	4196(5)	4139(6)
C(25)	−3255(4)	3308(5)	1835(6)

Discussion

Polarographic[6] and ¹H-n.m.r.[5] studies in solution support a significantly greater contribution from the quadrupolar form (II) to the structure of the pyrrolidino-quinone (5) than to its piperidino-analogue (6). The crystal structures of these molecules show similar results in the solid state, as shown in Table 3.

It can be seen quite clearly in Table 3 that the four bonds concerned in the conjugated system, N(2)-C(2)-C(3)-C(1')-O(1'), alternately increase or decrease in length, down the series, 5, 6, 3, and 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 each of the first three compounds. The N(2)-C(2) bond length for 5 is the shortest of the series and a relatively high degree of sp² hybridization of N(2) is thus apparent. Consequently, there is increased electron delocalization within the benzoquinone moiety itself; C(2)-C(3) lengthens, C(3)-C(1') shortens, and C(1')-O(1') lengthens. This trend occurs in all three substituted benzoquinones considered, but to a decreasing extent down the series, 5, 6, and 3.

The aziridino-quinone (3) has by far the least contribution from (II) since its N(2)-C(2) bond length is much nearer to that of a single bond than for 5, and its benzoqui-
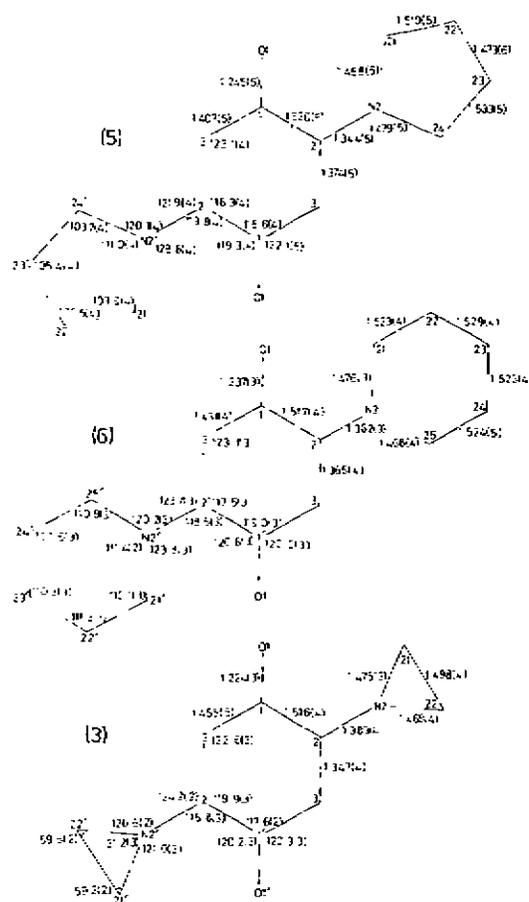

Fig. 2 Bond lengths (Å) and angles (°) of 2,5-bispyrrolidino-1,4-benzoquinone (5), 2,5-bispiperidino-1,4-benzoquinone (6), and 2,5-bisaziridino-1,4-benzoquinone (3).[9]

none bond lengths are very much closer to those of 1,4-benzoquinone. This implies that N(2) has a much higher degree of sp³ hybridization.

The bond lengths under consideration for the piperidino-quinone (6) fall between those for 5 and 3 in every case. This implies a more equal contribution from both forms (I) and (II) towards the structure of 6. This is apparent when the geometry about N(2) is considered. N(2) lies at 0,18 Å from the plane defined by its three bonded atoms, C(2), C(21), and C(25). Similarly, N(2) lies 0,02 Å from the plane through C(2), C(21), and C(24) in 5, and 0,59 Å from the plane through C(2), C(21), and C(22) in 3. Close approximation to sp² hybridization of N in 5 is apparent owing to the planarity of the group, and approximate sp³ hybridization of N in 3 is equally apparent, since a tetrahedrally disposed nitrogen lies, theoretically, 0,49 Å from the plane of three adjoining carbon atoms (the greater distance of N(2) from the plane in 3, compared to the theoretical expectation, is due to the small internal ring angle, 61,2°, of the aziridino-group). In the piperidino-quinone (6), the distance

Table 3 A comparison of selected bond lengths (Å) in 2,5-bisaminated-1,4-benzoquinones

NR₂	N(2)-C(2)	C(2)-C(3)	C(3)-C(1')	C(1')-O(1')	C(2)-C(1)
Pyrrolidino (5)	1.344(5)	1.374(5)	1.407(5)	1.245(5)	1.520(5)
Piperidino (6)	1.362(3)	1.366(4)	1.431(4)	1.237(3)	1.517(4)
Aziridino (3)[9]	1.383(4)	1.347(4)	1.455(5)	1.224(3)	1.516(4)
—[a]	—	1.322(8)	1.477(6)	1.222(8)	1.477(6)

[a] 1,4-Benzoquinone[10]

of 0,18 Å of N(2) from the plane confirms a mixture of sp^2 and sp^3 hybridization of N; sp^2 hybridization seems to be slightly more favoured.

The sum of the angles about N may also be considered as a guideline to the type of hybridization. In 5, the sum affords a figure of 359,9°, whilst in 6, this is reduced to 355,4°, which tends in the direction of the value of 328,5° expected for a formally sp^3 hybridized nitrogen. There are, however, other factors perturbing the angles about nitrogen. One is the effect of steric hindrance on the angle C(2)-N(2)-C(21) and the other is the restraint on the internal ring angle dependent on the size of the ring.

There is a strong steric interaction between C(21) and O(1) in both 5 and 6. Both C(2)-N(2)-C(21) angles are greater than expected for either sp^2 or sp^3 hybridization of N. The angle in 5 is 128,8° and that in 6, 123,8°. Despite the increase in angles, the C(21) ... O(1) distances are still substantially less than the sum of the van der Waals radii. C(21) ... O(1) in 5 is 2,697 Å and H(211) ... O(1) is 2,446 Å, which is on the limit of steric interference. Similarly, C(21) ... O(1) in 6 is 2,845 Å, whilst H(211) ... O(1) is somewhat shorter than in 5, having a close contact distance of 2,097 Å. Since N(2) in 5 is effectively sp^2 hybridized, C(21) lies in the same plane as N(2) and the benzoquinone moiety. In 6, however, N(2) has some degree of sp^3 hybridization and C(21) lies out of this plane. C(2)-N(2)-C(21) in 5 is substantially greater than in 6 since it requires a larger angle in the coplanar case to effect a required separation between C(21) and O(1) than it does in the non-coplanar case.

Brown has argued[13] that double bonds *exo* to five-membered rings are both less reactive and more stable relative to their saturated analogues, than are corresponding double bonds *exo* to six-membered rings. The greater contribution of (II) to 5 relative to 6 can be rationalized in terms of this argument.

The C(2)-C(1) bond length, which is not incorporated in the conjugated system, has been shown previously[3,8,14] to be longer for 2,5-bisaminated 1,4-benzoquinones than for 1,4-benzoquinone itself. These findings are confirmed by this work, as shown in Table 3.

The conformation of 5 is essentially planar, with the exception of C(22) and C(23) in the pyrrolidino-ring (Fig. 3). Parameters of pucker for five- and six-membered rings were obtained in the form of polar coordinates.[15] The total degree of pucker is described by the radial coordinate, Q, and the angular coordinates θ and φ (six-membered rings), or φ (five-membered rings) describe the shape of the ring. The conformation of the pyrrolidino-ring lies between a half-chair ($^4H_3$) and an envelope (^4E), where '3' denotes C(22) and '4', C(23). Its parameters of pucker are 0,30 Å and 276° for Q and φ respectively.

The benzoquinone ring in 6, as in 5, is essentially planar, whilst the piperidino-ring has a symmetrical chair conformation, ($^4C_1$), where '1' denotes N(2) and '4', C(23) (Fig. 3). Its parameters of pucker are $Q = 0,02$ Å, $\varphi = 135°$, and $\theta = 178°$. The angles subtended by the mean planes through the quinonoid and pyrrolidino- or piperidino-rings are 10° and 57° respectively.
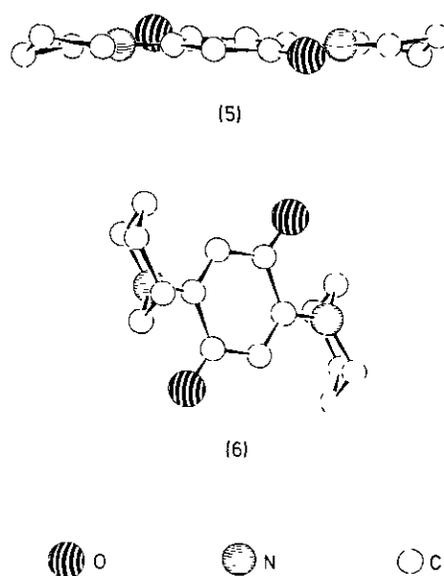

(5)

(6)

Fig. 3 Selected views of 2.5-bispyrrolidino-1,4-benzoquinone (5) and 2,5-bispiperidino-1.4-benzoquinone (6) to show the conformation of the pyrrolidino- and piperidino-rings.

There are no intermolecular close contacts in either structure.

All calculations were perfomed on a Univac 1106 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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