The Synthesis and Structure of a Macrocycle containing a Quinone Unit by Treatment of Tetrafluoro-1,4-benzoquinone with 1,11-Diamino-3,6,9-trioxaundecane

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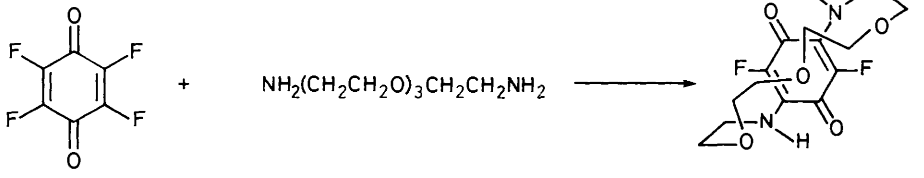
A one-step synthesis of a novel macrocycle containing a quinone unit by treatment of *p*-fluoranil with 1,11-diamino-3,6,9-trioxaundecane is described and its structure determined by a combination of *X*-ray crystallography, multinuclear NMR, IR, and UV-VIS spectroscopy.

Macrocycles containing quinone units have attracted considerable attention in recent years[1—5] since they offer a basis for the chromogenic or electrochemical detection of a variety of metal cations. The synthesis of such molecules, however, has required several steps, often involving the oxidation of a quinol unit within the macrocyclic system.[6] We report here a simple, one-step reaction for the preparation of quinone containing macrocycles in high yield together with a comprehensive structure determination by a combination of *X*-ray crystallography and molecular spectroscopy.



(1) (2) (3)

Table 1. ^1H and ^{13}C NMR data on (3) in $CDCl_3$ at 360 and 95.5 MHz, respectively.

^1H NMR/δ	Integration	Assignment
5.74—5.78 (br.)	2H	2 × NH
4.02 (m)	2H	$NCH_2 + OCH_2$
3.71 (d of t)	2H	
3.53 (m)	10H	
3.47 (m)		
3.35 (d of q)	2H	

^{13}C NMR/δ	DEPT[a]	Coupling/Hz	Assignment
171.85	0	AA'XX' (See text)	C=O [C(1) and C(4)]
171.79			
171.71			
171.66			
171.58			
171.52			
136.65 (d)	0	^1J_F 241	C(3), C(6)
134.81 (d of d)	0	^2J_F 4.3 ^3J_F 1.3	C(2), C(5)
71.09 (s)	Negative	0	C(9), C(17)
71.00 (s)	Negative	0	C(11), C(15)
70.87 (s)	Negative	0	C(12), C(14)
44.04 (q)	Negative	AA'XX' (See text)	C(8), C(18)

[a] DEPT = distortionless enhancement by polarisation transfer.

The reaction of fluoranil (1, 1×10^{-3} M) with 1,11-di-amino-3,6,9-trioxaundecane (2, 2×10^{-3} M) in toluene at ambient temperature overnight gave a deep red solution and a white precipitate of the hydrofluoride salt of (2). After washing with water, drying and concentrating the solution to 10% of the original volume, dark violet, lustrous crystals of (3) were obtained in 62% yield (not optimised),† m.p. = 172 °C. The IR spectrum of (3) as a Nujol mull showed absorptions at 3300 cm^{-1} (sharp N–H str.), 1675 (C=C str.) and 1600 (strong, C=O str.) and the UV-VIS spectrum (MeCN) revealed absorptions at λ_{max} = 594 nm (ε = 304 mol^{-1} l cm^{-1}) and λ_{max} = 358 nm ($\varepsilon = 2.05 \times 10^4$ mol^{-1} l cm^{-1}).

The ^{19}F NMR spectrum ($CDCl_3$) showed a single peak at −165.9 p.p.m. relative to $CFCl_3$ which remained unchanged down to −60 °C and the ^1H NMR data are summarised in Table 1. Although these data are clearly consistent with disubstitution of the quinone ring, they do not allow an unambiguous distinction between substitution in the 2,5-, 2,3-, or 2,6-positions. Chemical precedent however, implies that disubstitution would occur in the 2,5-positions[7] and the single crystal *X*-ray analysis confirms this structural assignment.‡

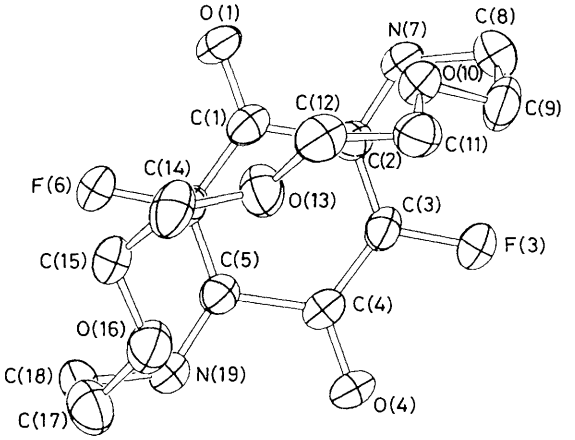


Figure 1. The *X*-ray crystal structure of (3) with C(1)—C(6) representing the quinone ring and C(8)—C(15) the carbons of the macrocyclic ring.

The molecular structure (Figure 1) shows the quinone ring to be substituted in the 2- and 5-positions, with the two remaining N–H bonds orientated towards the quinone oxygen atoms but too far away (*ca.* 226 pm) for strong hydrogen bonding. Figure 1 shows the molecule as seen normal to the quinone plane. If the molecule had C_2 symmetry, atom O(3) would be, in projection, at the centre of the quinone ring. In fact, it subtends an angle of 8° with the normal through the ring centre and hence, in the solid state, the molecule lacks an element of symmetry. Molecular models suggest, however, that in solution the molecule could be fluxional with the quinone ring able to pass through the loop of the macrocyclic system.

The interpretation of the ^{13}C NMR data§ which follows from the bond connectivity is then as follows. The carbonyl

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† Satisfactory elemental analysis was obtained. Parent peak, FAB MS 332; *M* ($C_{14}H_{18}N_2O_5F_2$) = 332.

‡ *Crystal data* for $C_{14}H_{18}N_2O_5F_2$ were collected on a Picker, four-circle diffractometer recently interfaced to an AT-TURBO 286 IBM-compatible microcomputer (full details to be published elsewhere) using Zr-filtered Mo-K_α radiation and pulse height analysis. Space group $P\bar{1}$, a = 9.626(5), b = 9.581(4), c = 9.558(5) Å, α = 103.64(4), β = 69.46(4), γ = 80.69(4)°; D_c = 1.43 g cm^{-3}, D_{obs} = 1.41 g cm^{-3}; Z = 2 molecules/cell. The structure was solved by direct methods using SOLVER.[8] A total of 1967 significant reflections were collected; R = 0.058; R_w = 0.062. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ High resolution ^1H and ^{13}C NMR data were obtained (in $CDCl_3$) on Bruker AM360 and WM250 MHz instruments using tetramethyl silane (TMS) as internal standard. ^{19}F NMR spectra were obtained on the WM250 instrument using $CFCl_3$ as internal standard.

signal centred at δ 171.68 is a six line pattern (*ca.* 5:1:3:3:1:5) characteristic of an AA′XX′ system (A = C, X = F) with J_{AX} 18.4, $J_{AX'}$ 9.7, $J_{AA'}$ 0, and $J_{XX'}$ 7.1 Hz as reproduced by PANIC simulation on a Bruker Aspect 3000 computer for a four-spin system. The signal at δ 136.65 is obviously due to C(3) and C(6) of the quinone ring (^1J_F 241 Hz) and the doublet of doublets at δ 134.81 is assigned to C(2) and C(5) with ^2J_F 4.3 and ^3J_F 1.3 Hz. There are three sets of OCH_2 carbons at δ 71.09, 71.00, and 70.87 and these data are readily explained by the macrocyclic ring being situated above the plane of the quinone ring as revealed by the *X*-ray analysis, making C(3) = C(6), C(2) = C(5), C(9) = C(17), C(11) = C(15), and C(12) = C(14). The signal for the NCH_2 carbons appears as a quintet (in both 250 and 360 MHz spectrometers) again due to an AA′XX′ pattern with $J_{AX}(^4J_F)$ 4.2, $J_{AX'}(^5J_F)$ 3.4, $J_{AA'}$ 0, and $J_{XX'}$ = 7.1 Hz.

In conclusion we believe that this work offers a novel entry to macrocyclic compounds containing quinone rings. Further studies are in progress to extend the scope of the synthesis and to evalaute the ability of these molecules to complex metal cations, by a combination of UV-VIS studies and cyclic voltammetry.

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