X-Ray Crystal Structure of the Novel Bis-quaternary Dispiro System Obtained from the Reaction of Morpholine with Hexakis(bromomethyl)benzene

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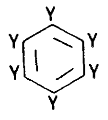
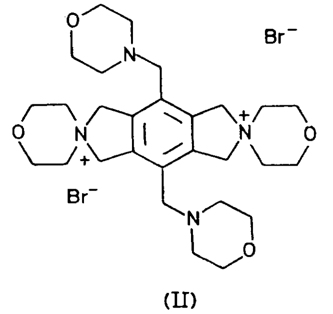
Summary In contrast to the six-fold substitution of hexakis(bromomethyl)benzene (Ia) by aniline to give the hexa-amine (Ib), reaction of (Ia) with morpholine occurs with dispiro-annelation yielding (II); the structure of this novel product was deduced spectroscopically and its detailed molecular geometry was determined by *X*-ray crystallography.



(I)

a, Y = CH_2Br
b, Y = CH_2NHPh



(II)

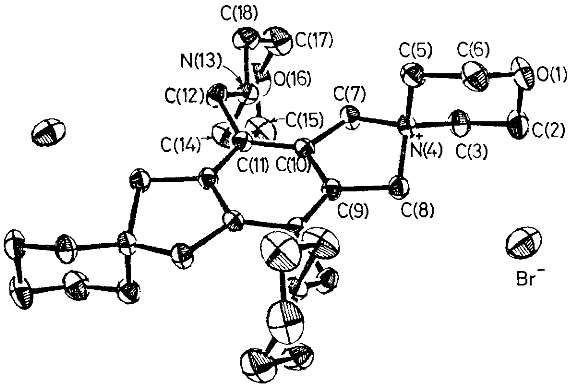


Figure. A view of the molecular structure of (II) in the crystal, looking onto the *ab* plane.

In recent studies[1] we have been concerned with the synthesis and inclusion properties of compounds with general structure (I). We now report a novel reaction discovered while investigating the substitution of hexakis(bromomethyl)benzene (Ia) with amines. Reaction of (Ia) in neat aniline for 27 h at 150 °C under N_2, followed by appropriate work-up, gave (Ib) in 47% yield, m.p. 214·5—215·5 °C (decomp.), which was characterised by microanalysis and i.r. and ^1H and ^{13}C n.m.r. and mass spectroscopy (full details will be given in a later publication). This six-fold substitution process is analogous to that found[2] in the base-catalysed reactions of (Ia) with alcohols, phenols, thiols, and selenols. However, reaction of (Ia) in refluxing morpholine under N_2 for 22 h, gave a moderate yield of a highly water-soluble product which was precipitated by addition of ethanol–water during the aqueous work-up. The high melting point of the product (colourless crystals, m.p. > 290 °C, from aqueous dioxan), its insolubility in organic solvents, and the formation of a AgBr precipitate with $AgNO_3$ in aqueous solution, are in keeping with an ionic structure; however, the presence of one or more quaternary nitrogen centres is suggested by the absence of N–H stretching band in the i.r. (KBr) spectrum, the solubility in presence of an excess of 5N NaOH, and by the ^{13}C n.m.r. spectrum (in D_2O) which is insensitive[3] to added base. The structure (II) was assigned to this product mainly on the basis of its microanalysis and spectroscopic evidence: ^1H n.m.r. τ[D_2O, internal reference $MeSi(Me_2)CH_2CH_2CH_2SO_3^-$ Na^+] 7·47 (8H, m), 6·38 (4H, s), 6·19 (16H, two overlapping m), 5·79 (8H, m), 4·79 (8H, s); ^{13}C n.m.r. (δ_C in D_2O), two aromatic carbon resonances at 134·4 (s) and 130·1 (s) p.p.m. (2:1), the remainder of the spectrum comprising signals at 67·4 (two superposed lines), 62·7, 60·6, 57·6, and 53·3 (all t in off-resonance ^{1}H decoupled spectrum).

Since (II) embodies the first example of a new heterocyclic dispiro ring system we have carried out a single-crystal *X*-ray diffraction analysis of this compound.

Crystal data: orthorhombic, space group *Pbca*, $Z = 4$, $a = 12{\cdot}49$, $b = 17{\cdot}13$, $c = 13{\cdot}78$ Å. The structure was solved by Patterson and Fourier methods employing 2229 independent reflections measured with Mo-K_α radiation on a Hilger and Watts automatic diffractometer, and has been refined to a final *R* factor of 0·029 (all 22 hydrogen atoms located).†

A view of the molecular structure of (II) is shown in the Figure, the molecule, located on a point of inversion, being constrained to have a centre of symmetry. The two independent morpholine rings both have chair conformations. An interesting feature of the molecule is the marked displacement of the quaternary nitrogen atoms above and below the plane of the central benzene ring (±0·47 Å). The bromide anion to quaternary nitrogen separation is 4·78 Å. Full details of the structural analysis will be given in a future paper.

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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 Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] D. D. MacNicol, A. D. U. Hardy, and D. R. Wilson, *Nature*, 1977, **266**, 611, and references therein.

[2] D. D. MacNicol and D. R. Wilson, *J.C.S. Chem. Comm.*, 1976, 494, and references therein; *Chem. and Ind.*, 1977, 84; D. D. MacNicol, A. D. U. Hardy, and D. R. Wilson, unpublished results.

[3] Significant changes in ^{13}C chemical shifts are expected if base-promoted deprotonation takes place at an ammonium centre; *cf.*, *e.g.*, J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972, p. 153.