N-Bridged Heterocycles. Preparation and Properties of 1,3-Polymethylenebenzimidazolium Salts and Related Systems

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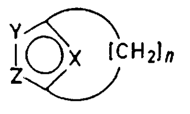
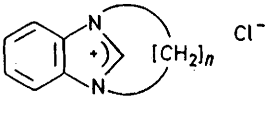
Summary A series of benzimidazolium chlorides, and benzimidazole-ones and -thiones with polymethylene chains of between 5 and 12 members linking the 1- and 3-positions have been made and their chemical and spectroscopic properties examined.

1,3-Bridged derivatives of various 5-membered heterocycles [*e.g.* (**1**)] have been prepared in recent years,[1–3] in some examples of which the lower limit of n is 6 or 7.† However, no examples have yet appeared in which hetero-atoms occupy the bridgehead positions. We herein report the first syntheses of such compounds, the benzimidazolium salts (**2**) and the benzimidazole-ones (**5**) and -thiones (**6**).

The synthesis of the necessary precursors to these compounds, the *NN′*-polymethylene-*o*-phenylenediamines (**3**; n = 4—12), are elaborated elsewhere.[5] While these compounds do not give benzimidazoles with carboxylic acids (the Phillips benzimidazole synthesis), they react readily with aromatic aldehydes to give the dihydrobenzimidazoles (**4**). These products, unlike their unbridged analogues, show no tendency to aromatise with mineral acid or electrophiles[6] and even with triphenylmethyl perchlorate undergo tritylation rather than aromatisation. However, the required salts (**2**; n = 6—12) are readily isolated in high yield when the amines (**3**) are treated with dichloromethyl methyl ether in hot dry tetrahydrofuran.[7] The lowest member of the series is not isolable in a pure state and slowly transforms into 1-(6-chlorohexyl)benzimidazole when left. The higher analogues smoothly undergo a similar ring-opening at elevated temperatures (⩾ 240°).


(1)

	X	Y	Z	ref
a	O	CH	CH	1
b	S	CH	CH	1
c	NH	CH	CH	1
d	CH	CH	O	2
e	CH	CH	S	2
f	CH	N	NH	3
g	CH	O	N	2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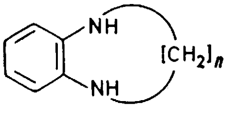
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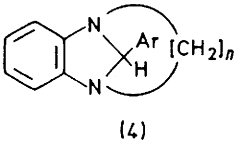
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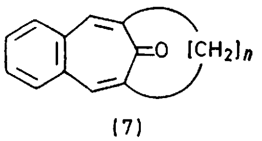
(7)


(a) (5; X = O) and (6; X = S) (b)

The spectroscopy of these compounds not only supports their structures but also underlines their aromaticity and the inherent strain in the lower members. Thus their u.v. spectra are characteristic of the benzimidazole chromophore, showing little variation in the wavelength maxima (210—211, 271, 278 nm) but a steady reduction in their extinction coefficients as n decreases. In the n.m.r. spectra, the 2-proton of the benzimidazolium ring is seen throughout at the characteristic low-field position (τ −1·5 to −2·2), and the methylene protons demonstrate the anisotropy associated with the aromatic system. Thus the heptamethylene-derivative (**2**; n = 7) shows a broad one-proton resonance at τ12·3 with similar but lesser upfield shifts in the other cases with n = < 12. The N-CH_2 resonance appears as a

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† A report[4] of a pyrrolo-analogue (**1**; X = NH; Y = Z = CH n = 4) was based on very flimsy evidence and we feel is probably incorrect.

triplet in the higher analogoes (**2**; $n = 12$—8) but shows non-equivalence of the geminal protons with $n = 6$ and 7, indicative of restricted swinging of the polymethylene chain.

From the diamines (**3**) were also obtained the benzimidazole-ones (**5**) and -thiones (**6**) by the action of phosgene and carbon disulphide respectively, the lower limit of n being 5. It is evident that these compounds are also potentially aromatic [*e.g.* (**5a**)$\longleftrightarrow$(**5b**)] and this fact should be verifiable from their spectra. The benzimidazolones show a sharp transition in their spectral behaviour below $n = 7$ indicative of a change from a planar aromatic structure (**5b**) to a non-planar, non-conjugated structure (**5a**). Thus the i.r. carbonyl stretching frequencies follow closely the observations of Kloster-Jensen and her co-workers[8] for the benzotropones (**7**) (of which our compounds are hetero-analogues), who concluded similar aromatic properties on this basis. The u.v. spectra again show little change in the absorption maxima (215—217, 234—232, 284—281·5, and 289—287 nm) with decreasing values of n, but show a steady decrease in the extinction coefficient of the two higher frequency absorptions [these results closely parallel those of the corresponding benzimidazolium series (**2**)]. This effect is particularly marked below $n = 7$. The i.r. and u.v. spectra of the thiones (**6**) are rather more difficult to interpret in that (i) the i.r. C=S stretching frequency is not as clearly seen and *decreases* as n increases, but shows a marked decrease below $n = 7$; and (ii) the u.v. spectra show complex variations of both absorption wavelength and extinction coefficient as n decreases, suggesting that two distinctive chromophores are associated with the planar (**6b**) and non-planar structures (**6a**).

The n.m.r. spectra do not add significantly to our understanding of this problem and will be discussed fully elsewhere. However, they show that 'swinging' of the polymethylene chain is restricted with compounds with $n \leqslant 10$ for the benzimidazolones and throughout the whole series of benzimidazolethiones, as indicated by the non-equivalence of the N-CH_2 protons. In the latter series, the higher members (**6**; $n = 10$ or 12) still show this non-equivalence even at 150 °C, while the analogous (**2**; $n = 10$ or 12) show complete equivalence even at -60 °C.

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