

BISMABENZENE AND ITS DIMER

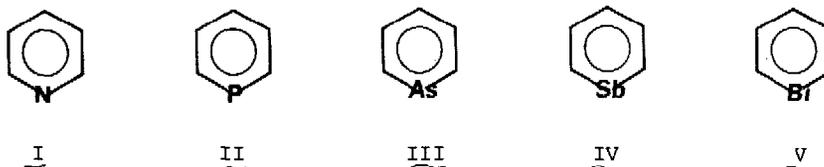
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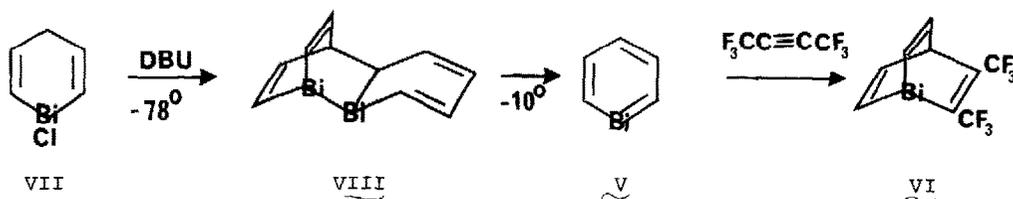
The group V heteroaromatic compounds, pyridine I, phosphabenzene II,² arsabenzene III,² stibabenzene IV³ and bismabenzene V⁴ form a unique series in which elements of an entire column are incorporated into aromatic rings. Although the first four members of the series are now available, the ultimate bismabenzene has been detected only *via* trapping to VI with hexafluorobutyne.⁴ We now wish to report on the direct spectroscopic detection of bismabenzene as well as its dimer.



Treating a THF solution of 1,4-dihydro-1-chlorobismabenzene VII with DBU causes exothermic loss of HCl and ultimately production of polymeric material. Under these conditions, we have been unable to detect bismabenzene.⁴ However, by using a non-volatile polyether solvent, such as tetraglyme, and applying a high vacuum, mass spectral peaks at m/e 274 (30) and 209 (100) can be detected. The moderate intensity of the molecular ion as well as its facile fragmentation to Bi are consistent with formation of bismabenzene.⁵ The He(I) photoelectron spectrum assigned to bismabenzene has been measured similarly.⁶

On the other hand treating VII with excess base (DBN, DBU or Dabco) at -78° in THF- d_8 causes immediate reaction with precipitation of the hydrochloride of the base. The $^1\text{H-NMR}$ spectrum⁷ illustrated in Figure 1 showed a clear but complex pattern at low field. The upfield portion of the spectrum was partially obscured by the residual THF protons and the excess base. Warming to -10° caused a reduction of intensity of this spectrum as well as the production of weak low field signals illustrated in Figure 3. Warming to room temperature caused broadening of all peaks and eventual destruction of all low field signals.

The very weak spectrum recorded at -10° (observable only via FT mode) shows the characteristic pattern of the group V heteroaromatics and we assign it to free bismabenzene. The α -protons occur as a doublet (J , 10 Hz) at τ -3.25 while the β -protons are a triplet at τ 0.14. The γ -proton at τ 2.30 is partially obscured by other peaks. The large progressive shift of the α -protons of I-V to low field is very striking. The α -protons of pyridine occur at τ 1.9, those of phosphabenzene at 1.4, arsabenzene at 0.7, stibabenzene at -0.7 and at -3.25 for bismabenzene. We associate this shift with the magnetic anisotropy of the increasingly large heteroatom.⁸



We feel that the low temperature spectrum (Figure 1) is consistent with a labile dimer of bismabenzene VIII. Thus the three vinyl protons α to Bi (H_2 , H_6 and H_8) are expected as low field doublets (at τ 2.49 (J , 11 Hz) and overlapping doublets at τ 3.10 (J , 11 Hz). The three-proton multiplet at τ 3.78 is assigned to the three vinyl protons β to Bi (H_3 , H_5 and H_9). The relatively sharp two-proton signal at τ 4.42 has a chemical shift similar to the olefinic protons of cyclohexadiene (τ 4.22⁹) and is assigned to H_{10} and H_{11} . The clear one proton triplet of doublets (J , 7, 4 Hz) at τ 5.63 is assigned to the diallylic bridgehead proton at C_4 . The proton at C_{12} was not observed and must occur under one of the upfield peaks. Double irradiation indicates that the peaks at τ 2.49, 3.10 and 5.63 are coupled to the τ 3.78 multiplet but not to each other.

In order to confirm this assignment 1,4-dihydro-1-chlorobismabenzene-3,5- d_2 was synthesized from the reaction of 1,4-pentadiyne with dibutyltin di-deuteride, followed by reaction with BiCl_3 . On treatment with DBU at -78° ,

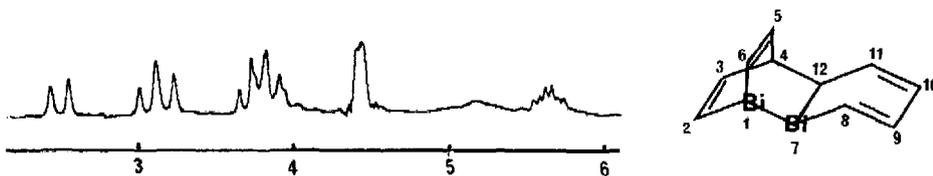


Figure 1. The H-NMR Spectrum of the Dimer of Bismabenzene.



Figure 2. The H-NMR Spectrum of the Dimer of Bismabenzene-3,5-d₂.

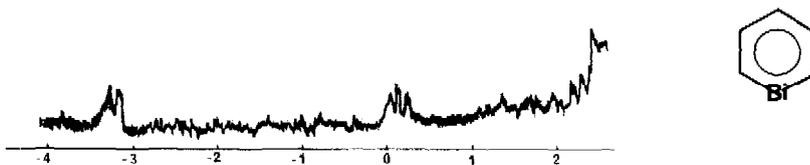


Figure 3. The H-NMR Spectrum of Bismabenzene.

the spectrum in Figure 2 was obtained. As expected the τ 3.78 multiplet is missing and the τ 4.42 signal is reduced in intensity. Coupling of the other signals to the β -hydrogens is eliminated.

The thermal lability of dimer VIII is hardly surprising. The dimer contains a Bi-Bi bond, of unknown but suspect bond strength,¹⁰ and can form two aromatic rings by an "allowed" Alder-Richart cleavage. The question whether the dimer is formed by the low temperature Diels-Alder reaction of two bis-m-benzene molecules or by reaction of some prior intermediate cannot at present be answered.

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References and Notes

1. A. P. Sloan Fellow, 1973-1976.
2. A. J. Ashe, III, J. Am. Chem. Soc., **93**, 3293 (1971).
3. A. J. Ashe, III, J. Am. Chem. Soc., **93**, 6690 (1971).
4. A. J. Ashe, III and M. D. Gordon, J. Am. Chem. Soc., **94**, 7596 (1972).
5. The Bi⁺ peak is frequently the base peak in the mass spectra of organo-bismuth compounds. See: D. E. Bublitz and A. W. Baker, J. Organometal. Chem., **9**, 383 (1967).
6. The PE spectrum were determined from solutions of polyethylene glycol monomethyl ether with an average molecular weight of 350. See the following paper: J. Bastide, E. Heilbronner, J. P. Maier and A. J. Ashe, III, Tetrahedron Lett., submitted for publication.
7. NMR spectra were recorded using a JEOL-RS-100 spectrometer using both FT and CW mode.
8. For pyridine see: J. D. Baldeschweiler and E. W. Randell, Proc. Chem. Soc., London, 303 (1961).
9. R. Burton, L. Pratt and G. Wilkinson, J. Chem. Soc., 594 (1961).
10. For tetraphenyldibismuthine, see: R. E. Dessy, P. M. Williams and R. L. Pohl, J. Am. Chem. Soc., **88**, 5117 (1966); R. E. Dessy, T. Chivers and W. Kitching, ibid., **88**, 407 (1966).