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THE CRYSTAL AND MOLECULAR STRUCTURE OF A 1,3-DIAZA-2,4-DIBOROLIDINE DERIVATIVE

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We report the X-ray diffraction structure determination of 1,3-di-p-chlorophenyl-2-triethylcarbinyl-4-ethyl-5,5-diethyl-1,3-diaza-2,4-diborolidine, II (2a). Previously obtained physical and analytical data on compound II are consistent with the structure formulated as 1,3-di-p-chlorophenyl-2,4-bis(triethylcarbinyl)-1,3-diaza-2,4-diboretidine (3). The present study was subsequently undertaken in order to obtain more conclusive evidence, and as part of a continuing collaboration (3b) to determine fundamental chemical and structural information about aminoboranes.

Using photographic anddiffractometer X-ray data, the compound II crystals were found to be tetragonal, with a = 16.943 ± 0.008, c = 9.599 ± 0.005 Å at approximately -125°C and with four molecules per unit cell. The space group, $P4_2/m$, was initially distinguished from $P4_2$ by intensity statistics and later confirmed by attempting refinement in both space groups. Intensity data corresponding to the unique portion of the full copper sphere were collected with MoKα radiation on a Datex automated G. E. Diffractometer. All data were collected at low temperature by cooling the crystal with a conventional nitrogen vapor cold stream. The structure was solved independently by Patterson map analysis and by application of the Sayre equation using the multiple solution program of Long (4). Least-squares refinement has reached a residual, $R = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$, of 0.084 for the 1819 independent intensities with $I_{obs} \geqslant 2.33\sigma_I$, where σ_I is the standard error of I_{obs} based on counting statistics.

The molecular structure contains a heterocyclic five-membered ring which is

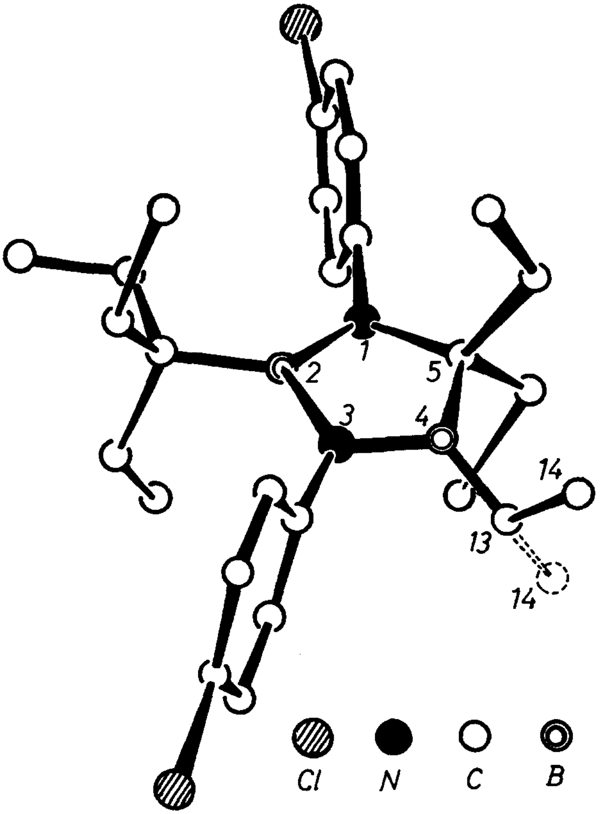
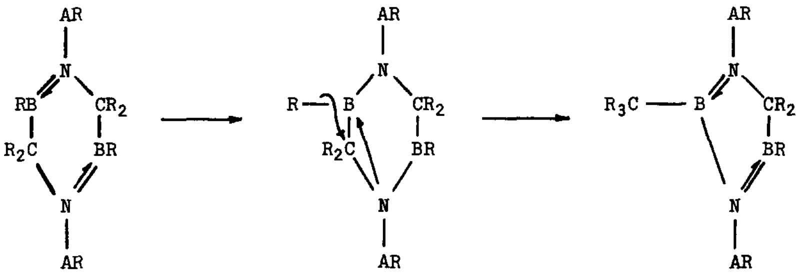


Fig. 1

The molecular structure. The molecule lies in a crystallographic plane of symmetry which contains the heterocyclic ring and bisects the phenyl rings. The ethyl group on atom B_4 is disordered such that atom C_{14} randomly occupies positions above and below the plane. Hydrogen atoms have been deleted for clarity.

isoelectronic to cyclopentadiene in the carbocyclic system. Crystal symmetry requires the molecule to have m-C_s symmetry, which is pseudosymmetry due to disorder, above and below the plane of the heterocyclic ring, of the ethyl group on atom B_4 (Fig. 1), the other ethyl groups being symmetrically located above and below the plane. The temperature factors indicate that all of the ethyl groups are undergoing considerable thermal motion even at -125°. Bond lengths in the heterocyclic ring are N_1-B_2 = 1.430 ± 0.010, B_2-N_3 = 1.505 ± 0.010, N_3-B_4 = 1.411 ± 0.011, B_4-C_5 = 1.586 ± 0.012, and C_5-N_1 = 1.488 ± 0.011 Å. When compared to standard (5,6) single B-N bond lengths of 1.56-1.64 Å, and double bond lengths of 1.35-1.36 Å, our results would indicate the presence of a small degree of conjugation and extensive delocalized π-bonding for the tricoordinate boron and nitrogen atoms. The infrared spectrum previously reported (3a) shows strong absorptions at 1481, 1449 and 1387 cm^{-1}. The two strong absorptions at 1481 and 1387 cm^{-1} should probably be assigned to stretching of the 1.41-1.43 and 1.50 Å B-N bonds. The planes of the phenyl rings, averaged over time and all molecules in the crystal, are required by symmetry to be strictly perpendicular to the heterocyclic ring and the temperature factors indicate relatively small amplitudes of vibration from the mean positions. Consequently the nitrogen p-orbitals are perpendicular to the adjacent carbon p-orbitals preventing effective π-overlap (7,8), as was indicated in the ultraviolet spectral data (3a). The average N-C, B-C, Cl-C, and aromatic C-C bond lengths are all normal. The average C-C single bond length of 1.58 Å is somewhat long, however the uncertainty in these is correspondingly large due to the large thermal motion and disorder in the ethyl groups mentioned above.



I

II

Fig. 2

R = C_2H_5; AR = p-ClC_6H_4, C_6H_5

Witte (13) has formulated a similar product due to isomerization of I (AR = C_6H_5) in the presence of aluminum chloride. It is therefore highly probable that the two reactions have analogous rearrangement steps (Fig. 2) above.

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(1) Author to whom correspondence should be addressed.

(2) Other nomenclature (a) for the ring system, compound I, 2,5-diborapiperazine (b) for the ring system, compound II, 2,4-diboraimidazolidine or 1,3,2,4-diazadiboracyclopentane. We have used the UPAC nomenclature for heterocyclic rings containing nitrogen, which seems to be preferred for B-N cyclic compounds, although all of the above nomenclature was found in the current literature.

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