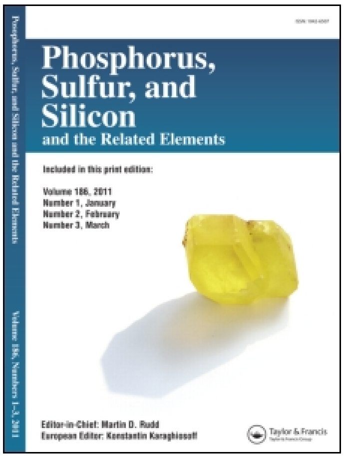

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Deformation Electron-Density Distributions of Tetraazathiapentalenes with Hypervalent S-N Bonds

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DEFORMATION ELECTRON-DENSITY DISTRIBUTIONS OF TETRAAZATHIAPENTALENES WITH HYPERVALENT S-N BONDS

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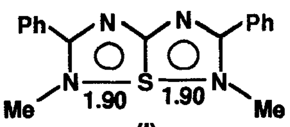
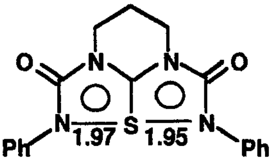
Abstract The deformation electron-density distributions of 6a-thia-1,3,4,6-tetraazapentalene derivatives (**I**, **II**) and bis(phenylthio)dibenzothiophene (**III**) were investigated by the X-ray diffraction method. For **I** and **II**, a structure around the hypervalent S atom is a trigonal bipyramid with equatorial sp^2 hybrid of S-C bond and lone-pair electrons and apical polarized S-N bonds. In **III** lone-pair electron densities are observed perpendicular to the thiophene ring and the C-S-C sulfide planes.

INTRODUCTION

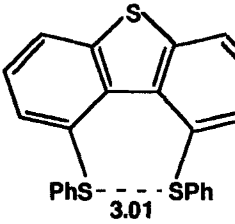
The electron-density distributions of 6a-thia-1,3,4,6-tetraazapentalene derivatives **I** and **II** were investigated by the X-ray diffraction method in order to shed light on the characteristics of hypervalent bonds. **I** and **II** are typical hypervalent sulfur compounds with symmetrical S-N bonds of 1.90 ~ 1.96 Å, which are longer than the normal single S-N bond (1.74 Å) by about 10 %.[1] Besides these typical hypervalent compounds, S···X (X=N, O, S etc.) nonbonding short contacts are often observed in organic sulfur compounds. Dibenzothiophene derivative **III** has a short intramolecular S···S contact of 3.012 Å.[2] The electron-density distributions of **III** was also studied to compare the electronic features of sulfur atoms.



(I)



(II)



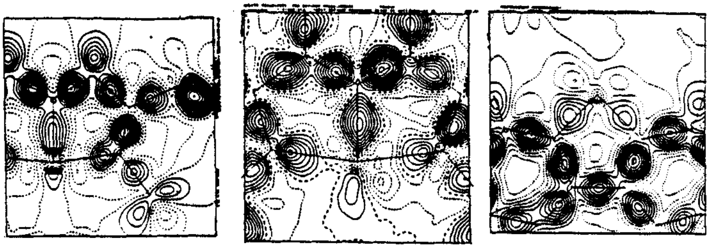
(III)

DISCUSSIONS

The 143 K data were measured on a RIGAKU-AFC5R diffractometer equipped with a liquid N_2 gas-flow device. The structure refinements were performed using multipole expansion atomic scattering factors[3] up to the hexadecapole expansion for S atom.

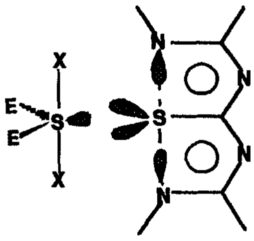
The final R values were 0.0334, 0.0335 and 0.0218 for **I**, **II** and **III**, respectively.

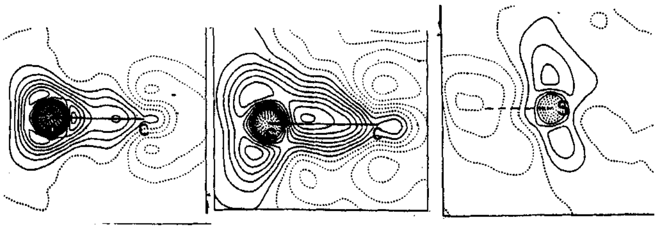
Figure 1(a) shows model-deformation maps[4] of the sections of the tetraazathiapentalene planes of **I** and **II** and the thiophene ring of **III**. For both **I** and **II**, positive electron densities along S-N bonds are observed near the N atoms, not in the center of the bonds. The net atomic charges derived from the multipole refinement suggest a polarized character of S-N bond. For each compound, two lone-pair electron densities are observed in the section perpendicular to the pentalene plane through the S-C bonds (Fig. 1(b)). The angles of C-S-L, C-S-L' and L-S-L' (L and L' = peaks of lone-pair densities) are about 120°. A structure around the hypervalent S atom is a trigonal bipyramid with equatorial sp^2 hybrid of S-C bond and lone-pair electrons and apical polarized S-N bonds as shown in the scheme. In **III** tone-pair electron densities are observed perpendicular to the thiophene ring and the C-S-C sulfide planes.



(I) (II) (III)

(a) The pentalene plane for I and II and thiophene plane for III





(I) (II) (III)

(b) Planes perpendicular to (a) through the S-C bonds for I and II and the bisection of CSC for III

Fig. 1 Deformation density Maps

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4. $\Delta\rho(\mathbf{r}) = \rho_{\mathrm{calc,multipole}}(\mathbf{r}) - \rho_{\mathrm{calc,spherical\ free\ atom}}(\mathbf{r})$