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Fujiko Iwasaki^a; Seui Kakuma^a; Satoshi Yoshida^a; Shin Murata^a; Masanori Yasui^a

^a Department of Applied Physics and Chemistry, The University of Electro-Communications, Tokyo, Ianan

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

FUJIKO IWASAKI, SEIJI KAKUMA, SATOSHI YOSHIDA, SHIN MURATA AND MASANORI YASUI Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu-shi, Tokyo 182, Japan

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 sp² 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

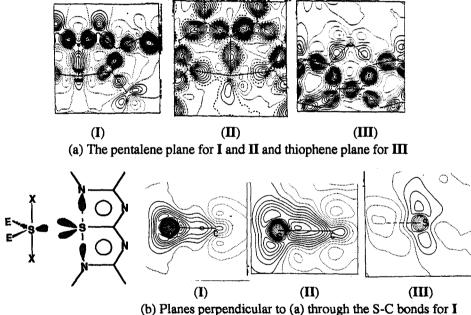
The electron-density distributions of 6a-thia-1,3,4,6-tetraazapentalene derivatives I and II were investigated by the X-ray diffraction method in order to shed light on the characteristics of hypervalent bonds. I and II are typical hypervalent sulfur compounds with symmetrical S-N bonds of $1.90 \sim 1.96$ Å, which are longer than the normal single S-N bond (1.74 Å) by about 10 %. 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. The electron-density distributions of III was also studied to compare the electronic features of sulfur atoms.

DISCUSSIONS

The 143 K data were measured on a RIGAKU-AFC5R diffractometer equipped with a liquid N₂ gas-flow device. The structure refinements were performed using multipole expansion atomic scattering factors³ 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 maps⁴ 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 sp² 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.



and II and the bisection of CSC for III

Fig. 1 Deformation density Maps

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- 3. N. H. Hansen and P. Coppens, Acta Cryst. A34, 909 (1978).
- 4. $\Delta \rho(\mathbf{r}) = \rho_{\text{calc,multipole}}(\mathbf{r}) \rho_{\text{calc,spherical free atom}}(\mathbf{r})$