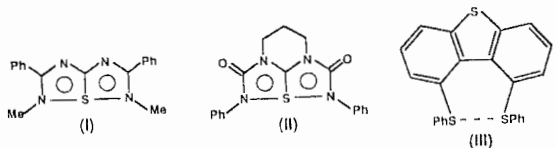
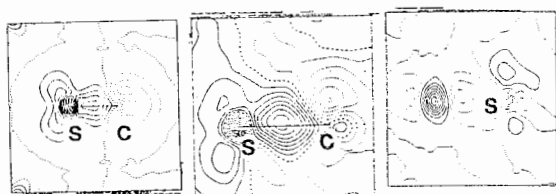


**OPS-04.03.07** CHARGE DENSITY DISTRIBUTION IN TETRAAZATHIAPENTALENES WITH HYPERVALENT S-N BONDS. By S. Kakuma\*, S. Yoshida, S. Murata, M. Yasui and F. Iwasaki, Dept. of Applied Physics and Chemistry, The Univ. of Electro-Communications, Chofu-shi, Tokyo 182, Japan

Tetraazathiapentalene derivatives **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% (Iwasaki & Akiba (1984) Bull. Chem. Soc. Jpn., 57, 2584; Iwasaki, Murakami, Yamazaki, Yasui, Tomura & Matsumura (1991) Acta Cryst. C47, 998). On the other hand dibenzothiophene derivative **III** has not such a hypervalent bond but a weak intramolecular S...S contact of 3.012 Å. The electron-density distributions of these compounds were investigated in order to shed light on the character of hypervalent S-N bonds and to compare electronic features of these sulfur atoms. Intensity data were measured at 143K up to  $2\theta_{\max}=100^\circ$  ( $88^\circ$  for **III**) and the structure refinements were performed using multipole expansion atomic scattering factors up to the hexadecapole expansion for S atom. **I**, orthorhombic, Pbcn,  $a=14.433(3)$ ,  $b=9.220(2)$ ,  $c=11.236(2)$  Å,  $Z=4$ ,  $R=0.037$  for 6398 reflections; **II**, orthorhombic, Iba2,  $a=20.313(3)$ ,  $b=21.365(2)$ ,  $c=7.472(2)$  Å,  $Z=8$ ,  $R=0.036$  for 6617 reflections; **III**, monoclinic, P2<sub>1</sub>/n,  $a=17.650$ ,  $b=7.983(3)$ ,  $c=13.438(4)$  Å,  $\beta=94.57(3)^\circ$ ,  $Z=4$ ,  $R=0.023$  for 5442 reflections. In the model deformation maps of **I** and **II** residual peaks between S-N bonds are observed near the nitrogen atoms, while the bonding electrons of S-C bonds are elongated along the bonds. The net atomic charges derived from the multipole refinement suggest an electrostatic interaction between S and N atoms. Lone-pair electron densities are observed near the S atoms. In **III** the bonding electrons of S-C bonds are lower than those of C-C bonds. Lone-pair electron densities are observed perpendicular to the thiaphene ring and the C-S-C sulfide planes.



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



(b) Plane perpendicular to the plane (a) and including S-C for **I** and **II** or bisection C-S-C for **III**

Model deformation-density maps. Solid lines denote positive contours with interval  $0.05 \text{ e}\text{\AA}^{-3}$ .

**OPS-04.03.08** Charge Density Study of a Chromium Fischer Carbene Complex: A Study Based on Multipole Model Refinement and ab Initio CASSCF Calculation. By Kuan-Jiuh Lin, Hui-Jean Liu, Kin-Shing Chan and Yu Wang\*, Department of Chemistry, National Taiwan University, Taipei, Taiwan

A single crystal of chromium Fischer carbonyl carbene, methyloxy-2-phenylethynyl pentacarbonyl chromium,  $(\text{CO})_5\text{CrCC}(\text{OCH}_3)\text{C}\equiv\text{CC}_6\text{H}_5$ , was studied by X-ray diffraction at 110K and 300K. The space group of the crystal is monoclinic P2<sub>1</sub>/n and the cell parameters at 110K are  $a=11.383(1)$ ,  $b=11.506(1)$ ,  $c=11.739(1)$  Å,  $\beta=108.377(9)^\circ$  and  $Z=4$ . The bond distance between Cr and carbene carbon is 1.9990(4) at 110K. The electron density distributions of all the chemical bonds as well as the asphericity around Cr metal of the complex were investigated in terms of experimental X-X deformation density maps, the multipole model deformation density maps, and the theoretical deformation density distributions employing the ab initio HFSCF and CASSCF methods. The d-orbital occupancies of Cr atom can be derived from the multipole model and ab initio calculations. A better understanding of the Cr-carbene bond character is achieved by comparing the different electronic structures between HFSCF and CASSCF results via Natural Bond Orbital analysis. For chromium-carbene carbon double bond, the  $\sigma$  bond is considered to be an electron pair donation from an  $sp^2$  carbene carbon to a vacant chromium  $sd_\sigma$  orbital, while the  $\pi$  bond be the electron pair back-donation from a  $d_\pi$  orbital of chromium atom toward the vacant  $p_\pi$  orbital of the carbene carbon

(see Fig.). Such double bond can be expressed as  $\text{M}\overset{\ominus}{\text{C}}\overset{\oplus}{\text{C}}$ . Moreover, it is clear from the CASSCF calculation that the additional contribution of the "acyl" resonance structure is responsible for the delocalized  $\pi$ -bond character along Cr-C-O(R). In fact, the "acyl" resonance form from the excited state plays an important role on the reactive site (being at carbene carbon) of nucleophilic reaction. The 1,3-dipolar cycloaddition at the triple bond can be interpreted with the Frontier orbital concept.

