Summary

This project is a joint effort in the application of laser techniques in the study of important molecules in atmosphere –The synthesis of organic sulfur compounds and its photochemistry (II) (subproject no 4).

We have focused on the synthesis of novel heterocyclic-fused sultines, precursors for o-quinodimethanes, and their application in Diels-Alder reactions. In collaboration with professors Chen, I.-C. and Wang, N.-S., we also studied the laser flash photolysis (LFP) of these sultines. Preliminary results showed that a reactive intermediate was observe upon LFP, which we reported during the annual progress report. In the future we shall continue in studying the details of the photolysis of sultines.

When heated in the presence of [60]fullerene, the sultines all underwent extrusion of SO₂ and the resulting heterocyclic-o-quinodimethanes were intercepted as the 1:1 adducts in 53% to 84% yields. The temperature dependent ¹H-NMR spectra show a dynamic process of the methylene protons. The activation free energies determined for the boat-to-boat inversion (14.5 to 15.2 kcal/mol) are found to be lower than those obtained for other related carbocyclic analogues. Various temperature ¹³C-NMR spectroscopy also provides important information about the structure of cycloadducts and reveals interesting spectra and symmetry correlation.
Keywords: o-quinodimethanes, transient absorption spectroscopy, Sultines, Diels-Alder Reaction.

[60] fullerene derivatives have become the current focus of research in biological and material science because of its unique spherical structure and feasibility in bulk production. Among the many derivatization methods available, cycloaddition reactions have played an important role and the Diels-Alder adducts of C$_{60}$ were first obtained by Müllen et al using o-quinodimethane as diene. These highly reactive species, generated in situ from a variety of precursors, are efficiently trapped with [60] fullerene which gain extra stabilization due to the restoration of aromatic system.

Although o-quinodimethane I has been frequently been used for the derivatization of [60] fullerene, their heterocyclic analogues have been recognized only recently. Various methods for generating these highly reactive diene have been developed. Among them cheletropic elimination of SO$_2$ from hetero-aromatic-fused 3-sulfolenes has drawn the most attention. Quinoxalines are important naturally occurring heterocycles and are usually found to have biological and pharmaceutical activity. Finding an easy, high yield method for generating quinoxalino-o-quinodimethanes is thus of particular interest.

Previously unknown sultines were synthesized from the reaction of Rongalite with the known bis-(bromomethyl)-quinoxalines in 55-76% yield. The Diels-Alder reactions of these sultines with typical dienophiles lead to high yields of 1:1 and 1:2 adducts in good to excellent yields. Small amount of sulfolenes were also formed, however, they did not react with any of these dienophiles even at 210 °C in contrast with the high reactivity of corresponding sultines.

When C$_{60}$ was refluxed in o-dichlorobenzene for a variable period of time with a slight excess of the quinoxalino-fused sultines, the 1:1 cycloadduct was obtained in 53-84% yield.

In summary we have developed a high yield and regiospecific method for the synthesis of quinoxalino-fused derivatives of [60] fullerene. Among the other reported methods, our results give the best yields. Also it is important to note that none of the bis-adducts of [60] fullerene was detected (<1%) in the reaction studied here, which is in sharp contrast with those with o-quinodimethane I. Quinoxalino-fused sultines are useful synthons of hetero-o-quinodimethanes, they react at milder condition and give better yields than those of corresponding sulfolenes and dibromides.

四、計劃成果自評
本計劃大部份依原定計劃如期完成，可發表論文至少三篇。

五、參考文獻
1. This work has been presented in (a) The 16$^{th}$ International Congress of Heterocyclic Chemistry, Bozeman, Montana, August 10-15, 1997, Book of Abstracts, OP-V-13 and (b) The 216$^{th}$ National Meeting of American Chemical Society, Boston, August, 1998, paper no.