Pinol Dibromide (3α,4α-Dibromo-4β,7,7-trimethyl-6-oxabi-cyclo[3.2.1]octane, 9). *endo,endo*-6,7-Dibromocineole (8) was unchanged after refluxing in toluene for 24 h. In 48 h a 10% conversion to 9 was noted. In *p*-xylene (140 °C) 45% rearrangement was observed in 8 h and 75% after 24 h. In bromobenzene (154 °C) the rearrangement of 8 to 9 was essentially complete in 5 h.

The black bromobenzene solution resulting from heating 638 mg of dibromide 8 in bromobenzene for 5 h was chromatographed on 50 g of silica gel using hexane, 2% ether–hexane, and 4% ether–hexane as eluants to give 300 mg of pinol dibromide (9). After two sublimations in vacuo, dibromide 9 displayed mp 58–60 °C: NMR (CDCl₃) 1.22 and 1.41 (s, 6, (CH₃)₂CO), 1.83 (s, 3, CH₃CBr), 2.0–2.8 (m, 8), 4.30 (d, 1, -CHOC-), and 4.40 ppm (d of d, 1, $W_{1/2}$ = 30 Hz, CHBr); mass spectrum, *m/e* 310 (2.5), 231 (100), 133 (67), 125 (56), 123 (28), 93 (56), 81 (41) and 69 (36). Anal. Calcd for C₁₀H₁₆Br₂O: C, 38.46; H, 5.13; Br, 51.28. Found: C, 38.54; H, 5.21; Br, 51.40.

Pinol Dichloride (3α,4α-Dichloro-4β,7,7-trimethyl-6-oxabi-cyclo[3.2.1]octane, 11). Aliquots were periodically withdrawn from a refluxing solution of *endo,endo*-6,7-dichlorocineole (10) in bromobenzene and analyzed by NMR. After 18 h, 33% rearrangement to 11 had occurred. The mixture darkened appreciably after 100 h and even after 134 h (60% 11) the conversion to 11 was not complete.

A 534-mg sample of dichloride 10 was heated at 260–270 °C for 1 h with considerable foaming and discoloration. The mixture was cooled and washed through a short plug of Florisil with hexane and ether. A total of 380 mg of brown oil was recovered and GLC analysis using a 10% Carbowax column at 170 °C indicated the presence of 82% of 11 (retention time 14 min) and 18% of 10 (retention time 19 min).[9] A pure sample of dichloride 11 was obtained by GLC and showed: NMR (CDCl₃) 1.21 and 1.39 (s, 6, (CH₃)₂CO), 1.65 (s, 3, CH₃CCl), 1.8–2.8 (m, 5), 4.20 (d, 1, *J* = 6 Hz, CHO), and 4.35 ppm (m, 1, CHCl); mass spectrum (70 eV) *m/e* (rel intensity) 222 (24), 187 (100), 180 (14), 178 (18), 171 (7), 169 (17), 151 (21), 145 (24), 143 (48), 97 (38), 93 (43), 81 (37), and 43 (45). Anal. Calcd for C₁₀H₁₆Cl₂O: C, 58.81; H, 7.17; Cl, 31 87. Found: C, 54.11; H, 7.15; Cl, 32.03.

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(9) Dichlorides 10 and 11 were stable to these GLC conditions.

Carbon-13 Nuclear Magnetic Resonance Study of Iodine–Sulfide Charge-Transfer Complexes

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Charge-transfer complexes between iodine and alkyl or aryl sulfides have been known for some time now.[1b,c] Most of the studies hitherto have been concerned with the measurement of the formation constants utilizing spectrophotometric methods,[2] although one proton NMR study has been re-
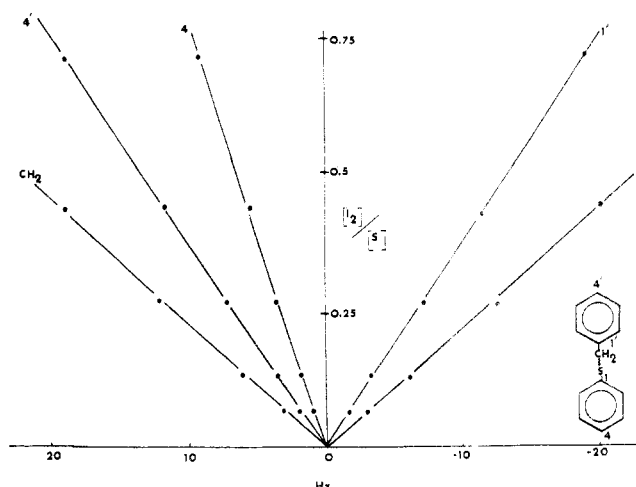

Figure 1. Plot of the ratio of iodine to sulfide concentration against the magnitude of the iodine-induced shift for benzyl phenyl sulfide.

ported.[3] While these investigations have presented useful information concerning the structural features which affect the strength of the charge-transfer interaction, they have not dealt with the gross molecular reorganization in these complexes. Since carbon-13 NMR chemical shifts are sensitive to changes in electron density[4] and the stereochemical relationship of atoms in a molecule,[5] it was felt that this spectroscopic method would provide additional insight into the electronic reorganization of the sulfides. In fact, Roberts has already shown that carbon-13 NMR spectroscopy can be utilized in the study of charge-transfer complexes.[6]

It is generally agreed that the sulfide–iodine charge-transfer interaction is a 1:1 species[2d] and that the sulfur–iodine bonds all lie in a straight line.[7] For the purpose of this report, all other species will be ignored. It has also been shown that in aromatic sulfides only the sulfur atom is complexed by the iodine.[2d]

A typical set of data is illustrated by the plot given in Figure 1. The plot is clearly monotonic, at least to molar concentrations less than 0.75, and this is a good indication that only one complexed species is present in solution.[8] Attempts at obtaining the limiting shift of the complex were not performed due to the insolubility of iodine under the experimental conditions. Attempts at decreasing the sulfide concentration (thus increasing the accumulation time significantly) facilitated some oxidation to the corresponding sulfoxide.

Given in Figure 2 are the carbon chemical shifts and iodine-induced chemical shifts (in parentheses) for the sulfides studied. The iodine-induced shifts were obtained directly from the plotted data by extrapolation of the Δδ vs. concentration curve to a 1:1 ratio. The value obtained by this method should be proportional to the limiting shift of the sulfide–iodine complex.[9]

The iodine-induced shifts in the aliphatic sulfides I, V, VI, and VII appear quite unexceptional. The α-carbon resonances suffer a large downfield shift due to the increase of the electron withdrawing nature of the sulfide–iodine complex vs. that of the free sulfide. The β-carbon resonances are shifted to higher field and this most likely results from a polarization of the C–H bond, the well known γ effect.[10] For the remaining sulfides II, III, and IV, the aliphatic α-carbon resonances are also shifted to lower field but to a lesser extent than the above compounds. However, for a directly bonded aromatic α-carbon the direction of shift is to *higher* field. An upfield shift is also observed for all ipso aromatic carbon resonances β to the sulfur atom. In aromatic systems there is a good correlation between the direction of the shift and electron density at a carbon site.[4]
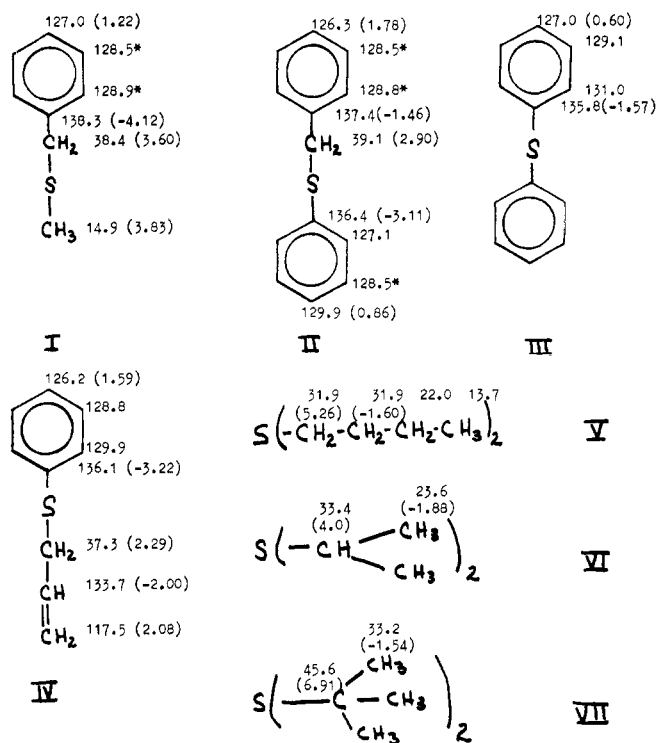
Figure 2. Carbon-13 chemical shifts and iodine-induced chemical shifts (slope of the δ_{obsd} vs. molar concentration plot) for the sulfides. *Assignments may be reversed.
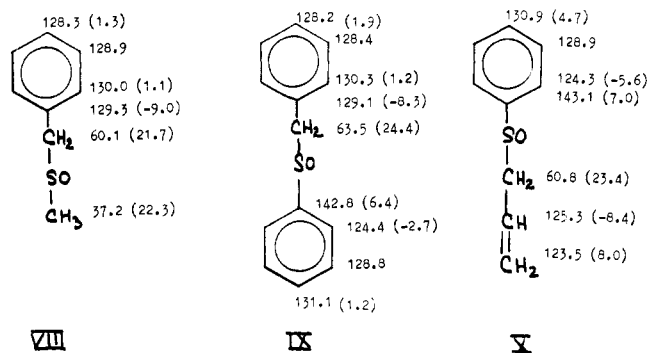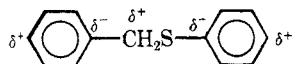

Figure 3. Carbon-13 chemical shifts and substituent chemical shifts (where negative values indicate upfield shifts) for the sulfoxides as compared to the sulfides.

An upfield shift would indicate an increase of electron density as compared to the parent sulfide. Except for compound IV, the only iodine-induced shift of any magnitude occurs for the para-aromatic ring carbons which invariably are shifted to lower field.

The net result of the iodine-induced shifts illustrated for compound II is shown below. The type of electronic interac-

tion found in the sulfide–iodine complex is best explained by a π-bond polarization mechansim.[11] Strong evidence supporting the π-bond polarization of these systems can be found in the induced shifts for the olefinic carbons in XI. Clearly, both of these carbon resonances are affected to the same degree but in opposite directions, as predicted by the π-bond polarization mechanism. Further support for the π-bond polarization mechanism can be seen in the substituent shifts of the sulfoxides VIII, IX, and X; see Figure 3.[12]

Experimental Section

All of the sulfides were commercially available and are estimated by VPC to be greater than 99% pure. The sulfoxides were obtained

from C. G. Venier, Texas Christian University, and were used as received. The iodine-induced shifts were obtained by an incremental addition of iodine to a 0.5 M solution of the sulfide in deuteriochloroform contained in a 10-mm o.d. NMR tube.

The carbon-13 magnetic resonance spectra were obtained in the Fourier transform mode on a JEOL FX-60 spectrometer system equipped with a 24K memory Texas Instruments computer. The spectra were obtained at an observing frequency of 15.03 MHz. General NMR spectral parameters were: internal lock to the deuterium containing solvent; a spectral width of 2500 Hz; a pulse width of 4 μm corresponding to a 36° pulse angle; and a pulse repetition time of 2.1 s. All shifts are estimated to be accurate to ±0.05 ppm and are referenced to internal Me$_4$Si.

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Studies on Friedel–Crafts Chemistry. 3. A New Preparative Method of 2-*tert*-Butyl-*p*-xylene by the AlCl$_3$–CH$_3$NO$_2$ Catalyzed *tert*-Butylation of *p*-Xylene with 2-*tert*-Butyl- and 2,6-Di-*tert*-butyl-*p*-cresol[1]

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There are few preparatively useful procedures for the synthesis of 2-*tert*-butyl-*p*-xylene (4) by the *tert*-butylation of *p*-xylene (1). The desired compound 4 was only obtained as