STEREOCHEMICAL AND A SINGLE-CRYSTAL X-RAY DIFFRACTION ANALYSIS OF 2,3,4,4a,6,10b-HEXAHYDRO-6-PHENYL-1,4-METHANO-1H-DIBENZO[b,d]THIOPYRAN: THE ADDITION PRODUCT FROM THE REACTION OF DIPHENYL THIONE AND NORBORNENE

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The adduct obtained from the reaction of diphenyl thione and norbornene, namely 2,3,4,4a,6,10b-hexa-hydro-6-phenyl-1,4-methano-1H-dibenzo[b,d]thiopyran, was subjected to a single crystal X-ray diffraction analysis. A syn relationship between the two protons on C(α) next to the sulfur atom was confirmed in the crystal state and suggests that an intermediate precursor of the adduct may not be formed by an entirely concerted process or a rearrangement occurs after a precursor is formed. If a [4 + 2]-cycloaddition had occurred, a rearrangement seems required to explain the stereochemistry of the adduct. ^{13}C and ^{1}H NMR analyses were performed and, using the HETCOR 2-D technique, it was possible to assign many signals with confidence although it was not possible to do so with every signal. Models were used to substantiate the assignments in the NMR spectrum as well as in the ultraviolet spectrum of the title compound.

INTRODUCTION

Our interest in the stereochemistry of multicyclic sulfur heterocycles[1] initiated a search several years ago for new methodology to obtain such systems. The recent[2] publication of the reaction of norbornene with diphenyl thione prompts us to reveal our results concerning the structure of the adduct formed. The condensation was carried out in boiling xylene and appeared to be complete within nine hours. We report herein an X-ray diffraction analysis of the adduct 1, the structure of which is shown in the projection drawing (Figure 1).
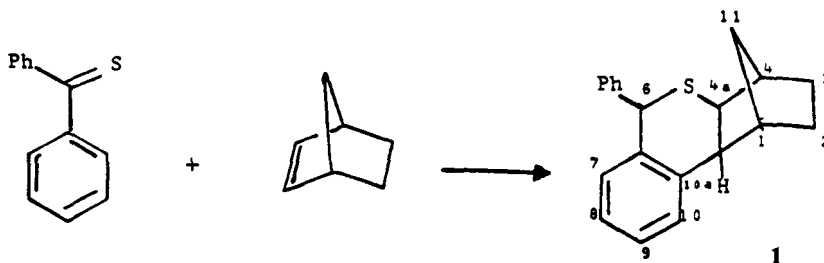
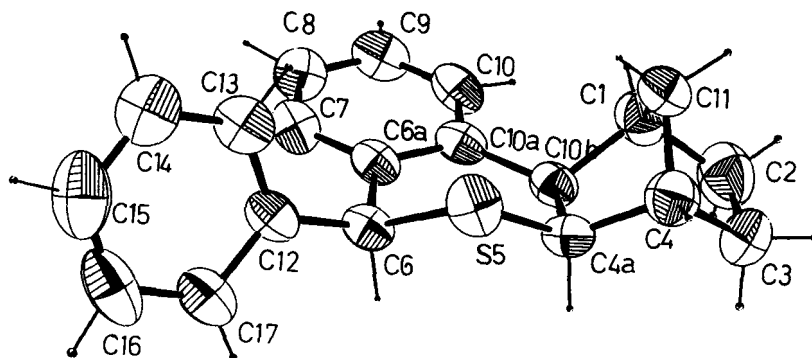*Author to whom all correspondence should be addressed.

FIGURE 1   Projection view of the sulfide 1.

RESULTS AND DISCUSSION

If the process is a [4 + 2]-cycloaddition of the Diels-Alder type, one can envision an intermediate as shown in **2**. Since the H(10a) is anti to the bridge protons in the intermediate, only a 1,3-sigmatropic shift would seem logical to restore the aromaticity found in the adduct **1**. However, such shifts are normally forbidden[3] but the high temperatures employed might allow such a transformation. Should this occur, H(6) in **1** would remain in an *anti* arrangement with respect to the bridge protons. This situation is *not* found in the structure of the single crystal but rather H(6) is *syn* to the bridge protons. Thus, we suggest that the addition may not be concerted or a rearrangement may ensue during the course of the reaction.
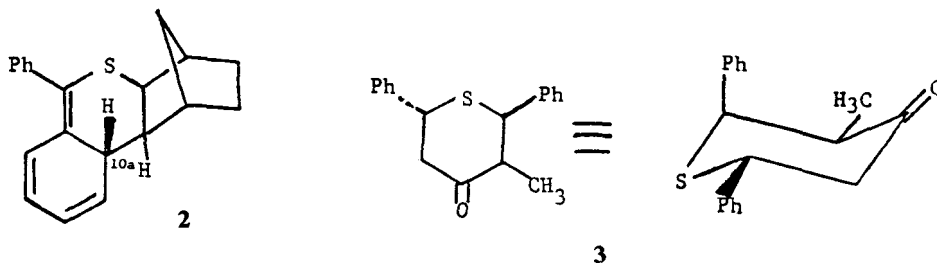
Interestingly, ultraviolet absorption maxima (in heptane) for **1** occurred at 223 nm ($\varepsilon = 8.85 \times 10^3$) with weak absorptions at 256.9, 262.2, 268.1 and 277 nm (Figure 2). In comparison, model *o*-xylene (in heptane) has maxima at 204, 210, and 215 nm ($\varepsilon = 5.60 \times 10^4$) with smaller peaks at 257, 263, 267, and 271 nm.[4] Model diphenyl thione has signals at 234 and 315 nm.[4] The other model system toluene has a maxima at 208 nm (hexane)[4] with smaller peaks in the range of 249–269 nm. Thus, the UV spectrum of adduct **1** is similar to the model systems as expected but has the largest maxima shifted to the longer wavelength possibly because of the strain imposed by the thiane ring present which is slightly flattened in the crystal structure.

Table I contains crystal data for **1** and Table II lists bond angles and bond distances. Ring A composed of C(4a), S(5), C(6), C(6a), C(10a), and C(10b) is a boat
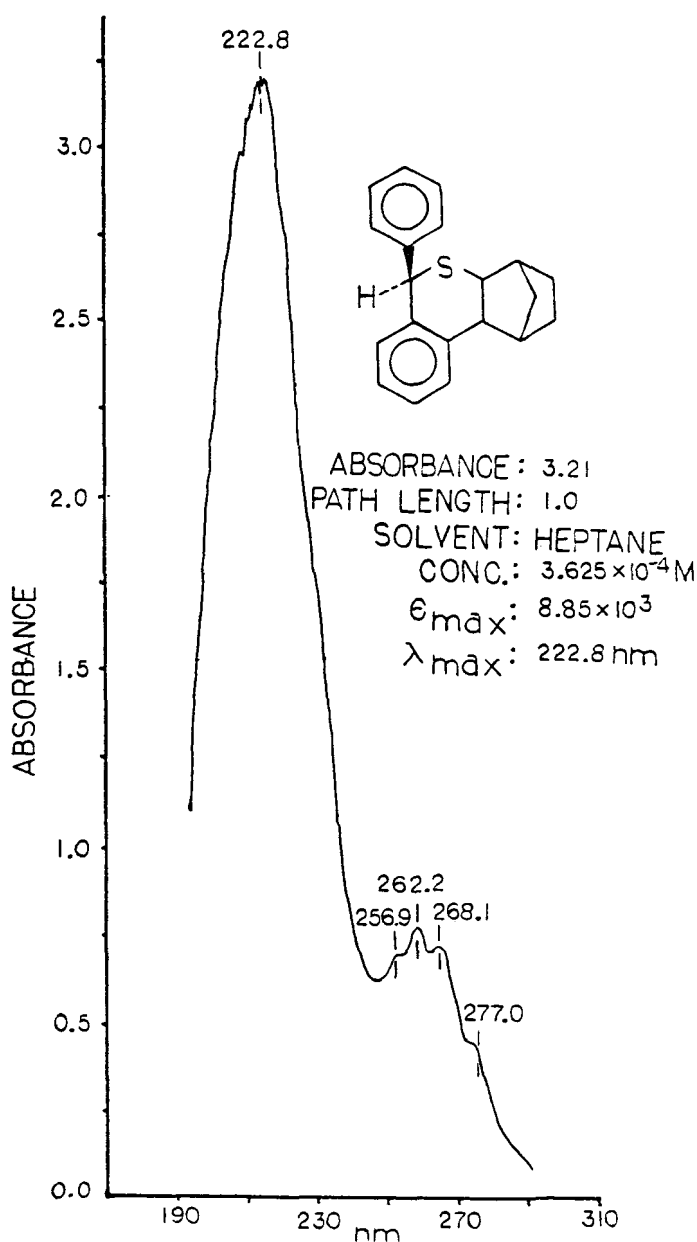
FIGURE 2 Ultraviolet absorption spectrum of 1.

conformer and flattened. Ring B composed of C(1), C(2), C(3), C(4), C(4a) and C(10b) is also a boat form and has some distortion because of the bridging by C(11). These rings are joined in a cis arrangement with H(4a) and H(10b) being *syn* to each other and also *syn* to H(6) which is geminal to the phenyl ring at C(6).

The C(6)–S(5) distance of 1.824(4) Å and that of C(4a)–S(5) of 1.810(4) Å are quite close to the mean distance given by Sutton[5] [C—S, 1.817(5)] Å for a number of

TABLE I

Crystal data for $C_{20}H_{20}S$ (1)

Formula	$C_{20}H_{20}S$
MWT	292.4
a	6.413(2) Å
b	15.727(5)
c	15.841(4)
α	90.0°
β	99.36(2)
γ	90.0
V	1576.3(8) Å^3
F(000)	624
μMoK_α	2.06
λMoK_α	0.71069 Å
D_{calc}	1.232 g cm^{-3}
Z	4
Obs. refl.	1636
R	4.8%
Space group	$P2_1/n$

TABLE II

Bond angles (°) and distances (Å) for $C_{20}H_{20}S$ (1)

C1–C2	1.517(7)	C2–C1–C11	101.6(4)
C1–C10b	1.564(6)	C2–C1–C10b	107.6(4)
C1–C11	1.525(6)	C10b–C1–C11	103.6(3)
C2–C3	1.532(8)	C1–C2–C3	102.8(4)
C3–C4	1.533(6)	C2–C3–C4	103.0(4)
C4–C11	1.522(7)	C3–C4–C11	103.0(4)
C4–C4a	1.540(6)	C3–C4–C4a	108.0(3)
C4a–S5	1.810(4)	C4a–C4–C11	101.4(4)
C4a–C10b	1.566(6)	C4–C4a–C10b	102.7(3)
S5–C6	1.824(4)	C4–C4a–S5	109.1(3)
C6–C6a	1.528(5)	S5–C4a–C10b	114.2(3)
C6–C12	1.514(5)	C4a–S5–C6	97.8(2)
C6a–C7	1.388(6)	S5–C6–C12	106.9(2)
C6a–C10a	1.405(5)	S5–C6–C6a	109.8(2)
C7–C8	1.387(6)	C6a–C6–C12	114.6(3)
C8–C9	1.376(6)	C6–C6a–C7	119.3(3)
C9–C10	1.368(7)	C6–C6a–C10a	121.3(3)
C10–C10a	1.407(6)	C7–C6a–C10a	119.4(4)
C10a–C10b	1.501(6)	C6a–C7–C8	122.0(4)
C12–C13	1.381(6)	C7–C8–C9	118.9(4)
C13–C14	1.381(6)	C8–C9–C10	119.8(4)
C14–C15	1.379(8)	C9–C10–C10a	122.8(4)
C15–C16	1.356(9)	C6a–C10a–C10	117.0(4)
C16–C17	1.387(7)	C6a–C10a–C10b	124.7(4)
C17–C12	1.397(6)	C10–C10a–C10b	118.1(3)
		C10a–C10b–C1	117.0(3)
		C10a–C10b–C4a	118.5(3)
		C1–C10b–C4a	101.4(3)
		C1–C11–C4	93.5(3)
		C6–C12–C13	121.3(3)
		C6–C12–C17	120.0(4)
		C12–C13–C14	121.4(4)
		C13–C14–C15	119.0(4)
		C14–C15–C16	120.4(5)
		C15–C16–C17	121.1(5)
		C16–C17–C12	119.3(4)

paraffinic C—S systems. More striking is the similarity of these distances in adduct **1** with the C(2)–S(1) and C(6)–S(1) distances found in the strained system *r*-2, *trans*-6-diphenyl-*cis*-3-methyl-4-thianone (**3**) and which were 1.830(6) Å and 1.815(6) Å, respectively.[6] Other distance and angles were unremarkable, in **1**.

^{13}C and ^{1}H NMR analysis of the adduct were of interest in view of the fact that the previous report[2] did not contain complete designation as to the stereochemistry in **1**. Utilizing both model systems and the HETCOR 2-D[7] technique, the following analysis was possible. Signals for ^{13}C which appeared at 127.3, 128.5 and 128.8 ppm were assigned to C(15), C(13,17), and C(14,16), respectively, on the basis of comparison studies with models **4**,[8] **5**,[9] and **6**, the latter being a theoretical system derived from the "principle of substitution additivity".[10] As can be seen from the formulas, the oxygen models **4–6** will, of course, cause the shift of the carbons to vary as compared to the analogous part in **1** containing a sulfur atom. However, the

128.8

127.3   128.5

             139.5

S

139.2

           141.7

1

128.6

127.0   125.3

            145.9

OH

CH_3

4

128.2

127.0   126.4

            143.7

OH

5

128.6

127.2   126.4

            143.7

OH

141.7

           146.5

6
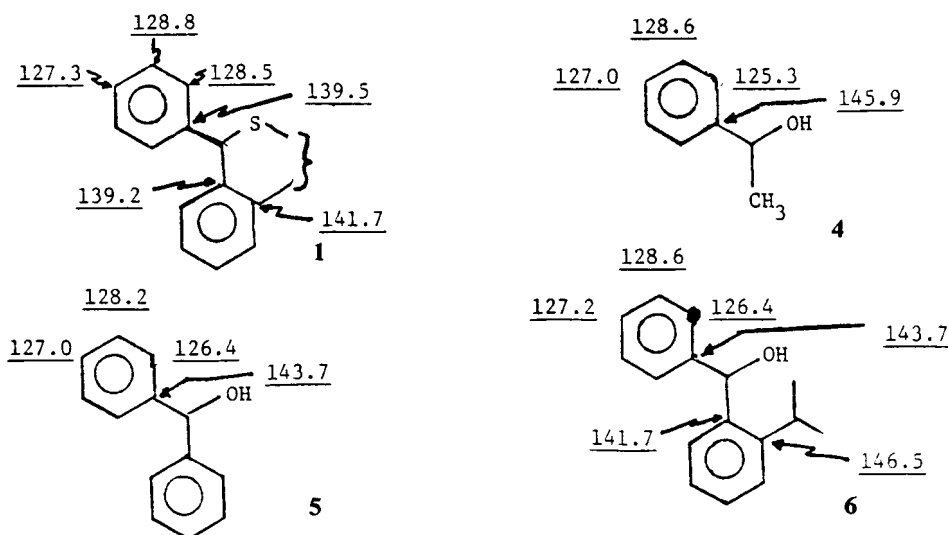
trend is quite clear in all systems. Moreover, the three signals shown above in **1** correlated in the HETCOR 2-D plot (Figure 3) with the aromatic protons which fell under a broad singlet in the ^{1}H spectrum at δ 7.33. This is the common pattern for monosubstituted phenyl systems.

Signals at 139.2, 139.5, and 141.7 ppm are for quaternary carbons in **1** as based upon analysis of the ^{13}C, proton-coupled spectrum. The "principle of substitution additivity" was used to resolve these signals with **6** as the model.[10] Thus, C(6a), C(10a), and C(12) are tentatively assigned to signals at 139.2, 141.7, and 139.5 ppm, respectively. Of course the oxygen atom causes the shifts to be greater in **4** than in **1** but this is to be expected.

The last four signals in the ^{13}C NMR spectrum for aromatic carbons showed unique features when compared with the ^{1}H spectrum in the HETCOR 2-D experiment. Two carbons correlated with two doublets in the ^{1}H spectrum at δ 6.62 and δ 7.45 while the other two carbons correlated with two triplets in the ^{1}H spectrum at δ 6.93 and δ 7.17. The two doublets must correspond to C(7) and C(10)
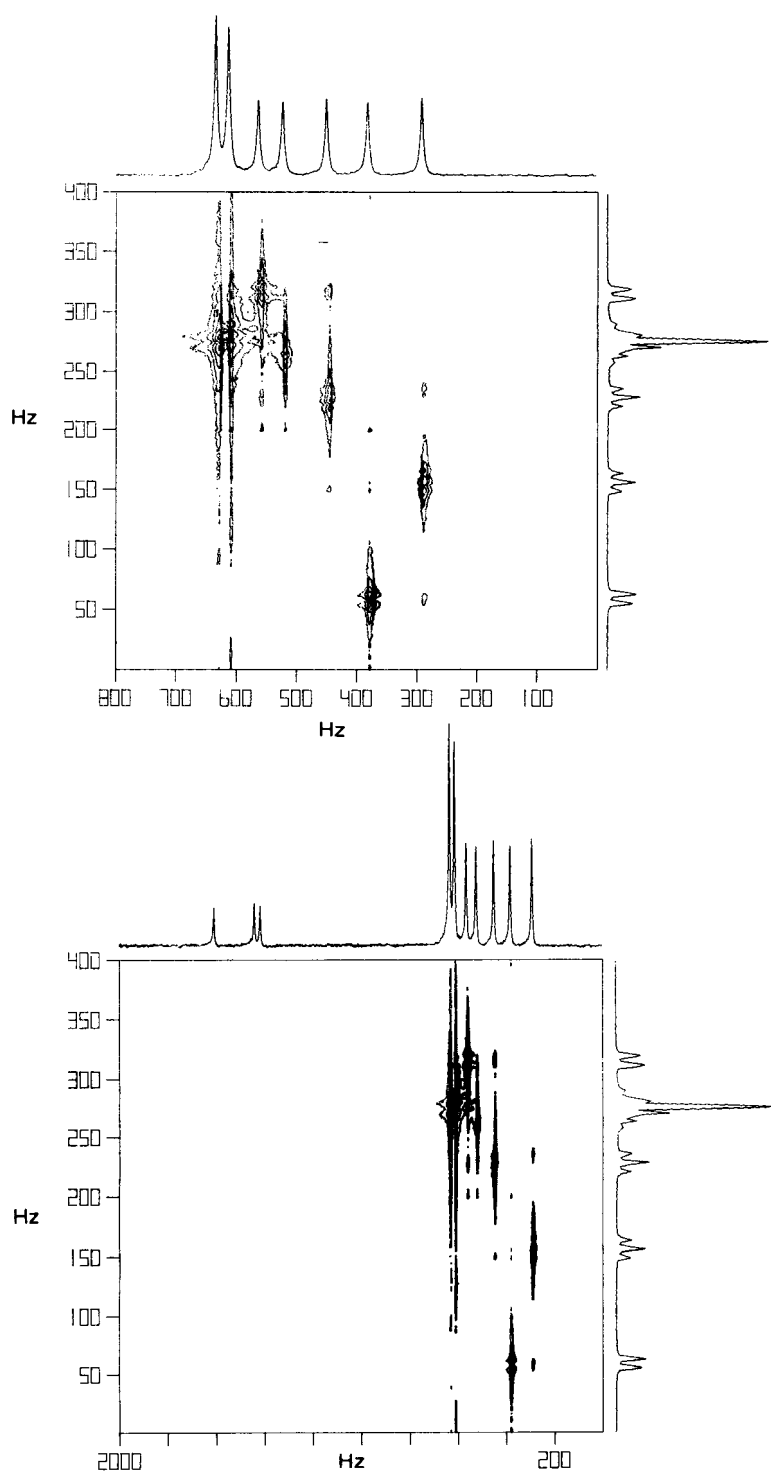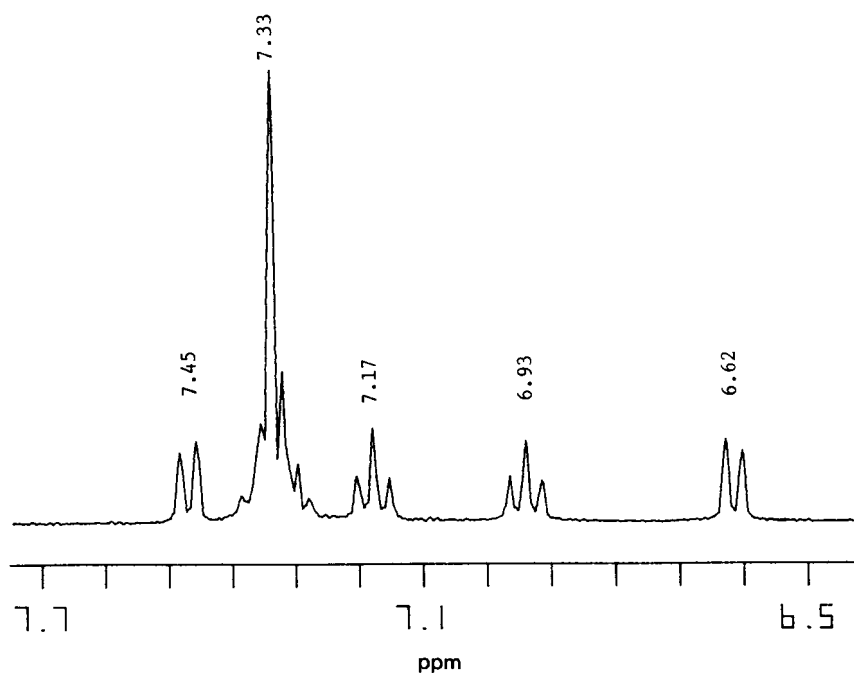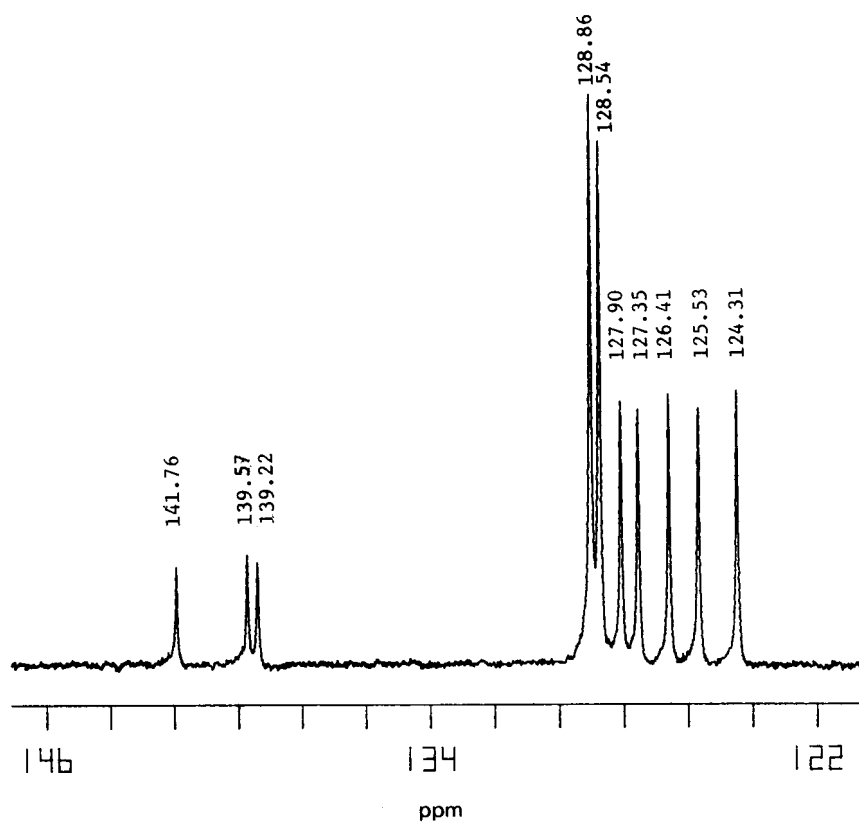
FIGURE 3   HETCOR 2-D plots of **1**. Spectrum (A) has the region from 0–800 Hz enlarged and spectrum (B) has the total composite plot. The ^{1}H and ^{13}C NMR spectra are shown on the right.

and the triplets to C(8) and C(10) but an unequivocal assignment for each *cannot* be made. The same situation persists for C(8) and C(9) but the ^{13}C signals at 124.3 and 126.4 ppm must correspond to these carbons although the individual assignments are not possible. Signals at 125.5 and 127.9 may be interchanged for C(7) and (10).

The remaining ^{13}C signals are in the aliphatic region for 1. Three model systems *exo*-2-hydroxynorbornane (7),[11] *exo*(2-hydroxy-3-methyl)norbornane (8),[11] and
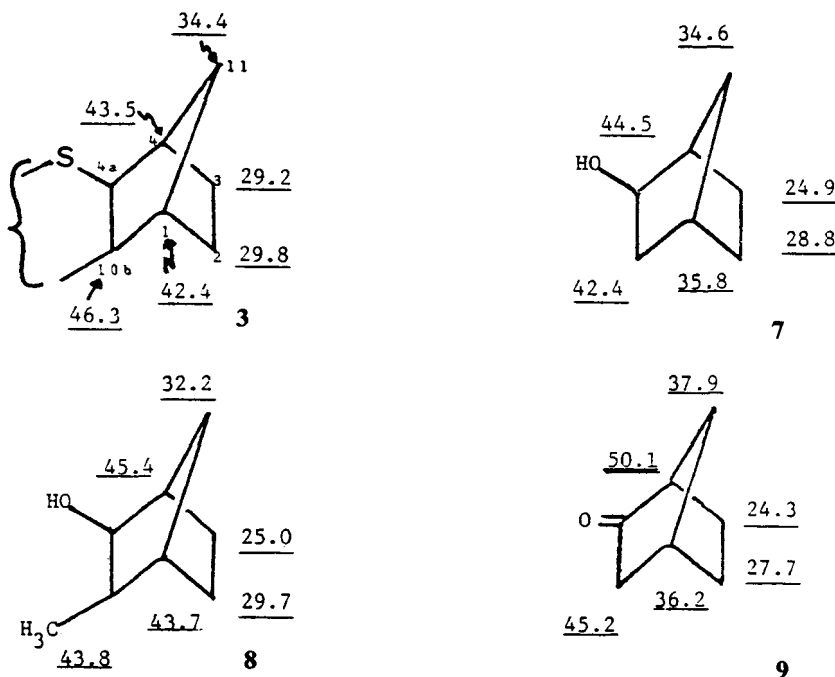
norbornan-2-one (9)[12] were used in the diagnosis of assignments for 1. Figure 4 is a HETCOR 2-D plot of the aliphatic region of the spectrum of 1.

Although the assignments for the counterparts of C(2) and C(3) in models 7–9 are in the literature,[11,12] we have no definitive method on which to base the values of 29.8 and 29.2 ppm, which we feel arise from these carbons in 1. Our tentative conclusion is that the multicyclic nature of the system in 1 may cause some distortion and thus the shifts for C(2) and C(3) cannot be unequivocally defined. However, the signal at 34.4 ppm in 1 for the bridge carbon follows nicely from comparison with the corresponding carbons in models 7–9. Shifts for bridgehead carbons C(1) and C(4) are also tentative but are based upon a similarity to the shifts in the models. One would expect the shift for C(4) to be less in 1 than for the corresponding carbon in the models because of the presence of oxygen in the models.

Analysis of the HETCOR 2-D NMR spectrum of 1 revealed that H(6) occurred at the lowest field (δ 4.77) in the aliphatic region of the ^{1}H spectrum but this did *not* correspond to the ^{13}C signal at lowest field in the aliphatic region of the ^{13}C NMR spectrum. The ^{13}C signal at 47.2 ppm did correlate with H(6) and was therefore assigned to C(6). Assuming that the broad doublets at δ 2.72 and δ 3.71 correspond
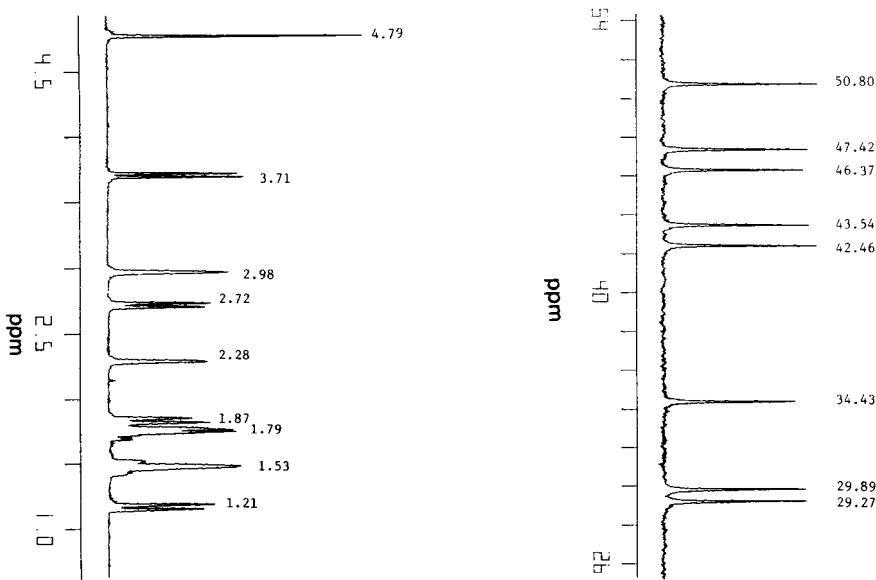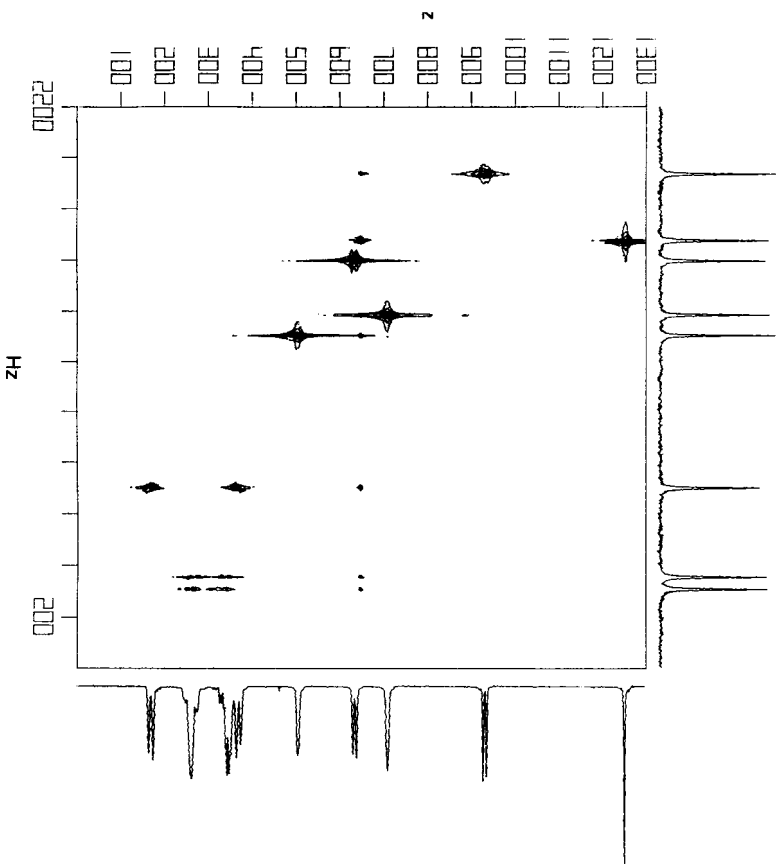
FIGURE 4   HETCOR 2-D plot of the aliphatic region of the ¹H and ¹³C NMR spectra of 1.

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to H(4a) and H(10b),[13] the assignment for C(4a) as the signal at lowest field in the aliphatic region (50.8 ppm) is apparent via a comparison with the ^{13}C spectrum of *exo*-2-norbornyl sulfide (10).[14] The ^{1}H NMR spectrum of 10 showed a signal for a proton attached to sulfur as a doublet of doublets of doublets and centered at δ 3.10. A second model *exo*-2-phenylnorbornane (11)[15] showed a triplet for the benzyllic proton at δ 2.72. In 1, the doublet at δ 2.72 for H(10b) did correlate with the ^{13}C signal at 46.3 ppm for C(10b). The doublet assigned at δ 3.69 to H(4a) correlated with the signal at 50.8 ppm for C(4a). The complete list of ^{13}C signals appears in the Experimental.

10   **11**

CONCLUSION

It is now clear that the addition of diphenyl thione to norbornene does *not* result in a simple adduct predictable by a classic [4 + 2]-cycloaddition process. In view of the *syn* arrangement of H(6) [alpha to S] to the bridging protons H(4a) and H(10b), it must be concluded that a different mechanism is operative or, if a [4 + 2]-cycloaddition occurs, a rearrangement must follow. The possibility exists that a [1,5]-shift could occur as shown starting from 2, but this would still necessitate a [1,3]-shift from 12 to yield 1. Our work clarifies the structure of 1 although the mechanism of its formation requires further study.
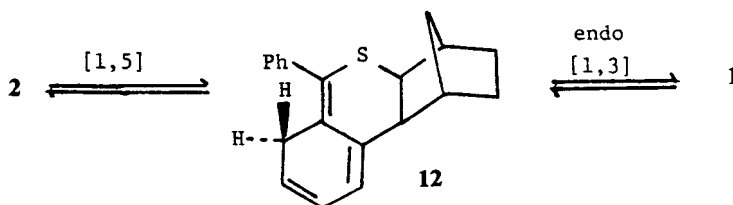
EXPERIMENTAL

General Data. All melting points are uncorrected using a Thomas-Hoover apparatus. The collection of ^{1}H NMR data was done on a Varian XL-300 spectrometer as was that for ^{13}C data. TMS was the external standard and DCCl$_3$ was the solvent. IR spectra were recorded on a Perkin-Elmer unit, model 681. Lawesson's reagent was obtained from Aldrich and used without purification, mp 223–226°C.

Diphenyl Thione. Benzophenone (3.64 g, 0.02 mole) and 6.07 g (0.015 mole) of Lawesson's reagent, 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide, were placed in 18 mL of anhydrous toluene (dried over sodium metal) under N$_2$. The reaction mixture was boiled until the ketone had been consumed as determined by TLC analysis (silica gel, petroleum ether/CH$_2$Cl$_2$ as eluent). The reaction time was 8 h. Evaporation of the solvent and chromatography of the residue over silica gel (petroleum ether/CH$_2$Cl$_2$ as eluent) gave intense blue crystals of diphenyl thione; 2.84 g (71.6%). mp 50–51°C (lit[7] 52–53°C); IR (KBr) 1250, 758, and 692 cm^{-1}. ^{13}C NMR ppm 127.9, 129.6, 131.9, 141.2, 238.4.

2,3,4,4a,6,10b-Hexahydro-6-phenyl-1,4-1H-dibenzo[b,d]thiopyran (**1**).   Diphenyl thione (0.74 g, 3.73 mmole), norbornene (0.47 g, 5.00 mmole), and 5 mL of anhydrous xylene (dried over sodium metal) were mixed under N_2. The reaction mixture was boiled until the diphenyl thione was consumed as monitored by TLC analysis. Evaporation of the solvent and chromatography of the product over silica gel (toluene as eluent) gave **1** which was recrystallized (ethanol) and melted at 107–108°C (lit[2] 108–109°C); yield, 0.31 g (28.4%). ^{1}H NMR δ 1.21 (d, 1 H), 1.53 (m, 2 H), 1.79 (m, 2 H), 1.87 (d, 1 H), 2.28 (bs, 1 H), 2.72 (d, 1 H), 2.98 (bs, 1 H), 3.71 (d, 1 H), 4.79 (bs, 1 H), 6.62 (d, 1 H), 6.93 (t, 1 H), 7.17 (t, 1 H), 7.33 (m, 5 H), 7.45 (d, 1 H); ^{13}C NMR ppm 29.27, 29.89, 34.43, 42.46, 43.54, 46.37, 47.42, 50.80, 124.31, 125.53, 126.41, 127.35, 127.90, 128.54, 128.86, 139.22, 139.57, 141.76. Mass spectral data on the molecular ion for $C_{20}H_{20}S$ (m/e) gave: Calcd 292.1287. Found: 292.1228. The procedure closely parallels that reported[2] with only slight differences in spectral data. Several experimental runs gave an average yield for **1** of 27.9%.

Crystal Data.   A crystal of $C_{20}H_{20}S$ was sealed in a capillary and mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least squared refinement of the best angular positions for fifteen independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation ($\lambda = 0.71069$ Å). Data (3603 points) were collected at room temperature using a variable scan rate, a θ–2θ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum, 2θ value of 116°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections and as the intensities of these reflections showed less than 8% variation, corrections for decompositions were deemed unnecessary. Data were corrected for Lorentz polarization and background effects. After removal of redundant and space group forbidden data, 1636 reflections were considered observed [I > 3.0 σ(I)]. The structure was solved by direct methods using MULTAN80.[16] Refinement of scale factor, positional and anisotropic thermal parameters for all nonhydrogen atoms was carried out to convergence.[17] Hydrogen positional parameters were determined from a difference Fourier synthesis. These hydrogen positional parameters and the associated isotropic thermal parameters were refined along with nonhydrogen parameters in the final cycles of refinement. The final cycle of refinement function minimized $\Sigma(|F_o| - |F_c|)^2$ led to a final agreement factor, R = 4.8% [R = ($\Sigma||F_o| - |F_c||/|F_o|$) × 100]. Scattering factors were taken from Cromer and Mann.[18] Unit weights were used throughout.[19]

ACKNOWLEDGMENT

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19. The atomic coordinates for this work are available upon request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The following data are deposited: fractional coordinates and anisotropic thermal parameters ($\times 10^4$ A^2) with e.s.d.'s in parentheses for the nonhydrogen atoms of **1**, fractional coordinates and isotropic thermal parameters ($\times 10^4$ A^2) with e.s.d's in parentheses for hydrogen atoms of **1**.