1-Azulyl Sulfides[1]

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The preparation and properties of some methyl and phenyl 1-azulyl sulfides are reported. It is pointed out that the spectral shifts of the visible band of azulene due to the methylthio and phenylthio groups in the 1- and 3-positions are inconsistent and violate some well-established rules. A discussion of these shifts is included.

The only azulyl sulfides previously known were aryl 1-azulyl sulfides, prepared by the reaction of an azulene with an arenesulfenyl chloride. Anderson and McDonald[3] obtained 1-(2,4-dinitrophenylthio)azulene from the uncatalyzed reaction of azulene with 2,4-dinitrobenzenesulfenyl chloride. Treatment of 4,6,8-trimethylazulene with 1 equiv. of benzenesulfenyl chloride gave 1-phenylthio-4,6,8-trimethylazulene (**1**), while the disubstituted product, 1,3-bis(phenylthio)-4,6,8-trimethylazulene (**2**), was obtained from the reaction of the azulene with 2 equiv. of the sulfenyl chloride.[4]

We were interested in preparing more 1-azulyl sulfides, including the alkyl 1-azulyl sulfides, because we thought they might show some interesting properties and because they could serve as precursors to other unknown sulfur derivatives of azulene, *viz.*, sulfoxides, sulfones, and sulfonium salts. It has been reported[5] that an aryl thiocyanate can be converted to the aryl methyl sulfide by treatment of the thiocyanate with an aqueous methanolic solution containing potassium hydroxide and methyl iodide.[6] This method appeared attractive as a route to methyl 1(3)-azulyl sulfides, since 1(3)-thiocyanoazulenes are easily prepared.[3] We have found that this synthetic method gives good to excellent yields of the desired methyl 1-azulyl sulfides. The reactions were generally carried out by adding excess alkali to a methanolic solution containing the thiocyanoazulene and excess methyl iodide kept under a nitrogen atmosphere. Methyl 1-azulyl sulfide (**3**) was obtained as a blue-green oil in 88% yield from 1-thiocyanoazulene.[3] 3-Thiocyanoguaiazulene (**4**) was prepared from guaiazulene (1,4-dimethyl-7-isopropylazulene) and thiocyanogen, and converted to the corresponding methyl sulfide, 3-methylthioguaiazulene (**5**), in good yield. Treatment of 4,6,8-trimethylazulene with thiocyanogen gave 1-thiocyano-4,6,8-trimethylazulene[7] (**6**) in 43% (74% net) yield and the previously unknown 1,3-dithiocyano-4,6,8-trimethylazulene (**7**) in 13% (23% net) yield. The dithiocyano derivative **7** is interesting in that it has two crystalline modifications: purple needles, m.p. 154.5–156°, and red needles. These crystalline forms are interconvertible; the more stable purple form can be obtained from solution by equilibrium crystallization, while the red form can be obtained by rapid removal of the solvent. Upon heating, the red needles undergo a transition to the purple form which then melts at about 155°. The monothiocyano derivative **6** was converted to the crystalline 1-methylthio-4,6,8-trimethylazulene (**8**) in 89% yield. Treatment of the dithiocyano derivative **7** with alkali in the presence of methyl iodide afforded the bissulfide 1,3-bis(methylthio)-4,6,8-trimethylazulene (**9**) as green needles, m.p. 97–98°. Another bissulfide, 1,3-bis(methylthio)azulene (**10**), was obtained from 1,3-dithiocyanoazulene[3] in a like manner.

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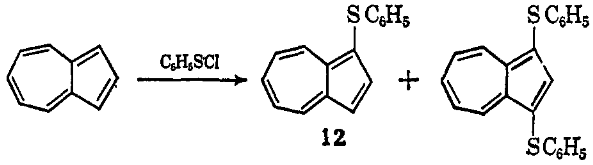
The identity of these methyl 1(3)-azulyl sulfides was shown by their satisfactory elemental analyses and their spectra. Infrared spectra showed the absence of any sulfur functional group which has a characteristic band in the infrared such as thiocyano, mercapto, sulfoxide, or sulfone. Also the n.m.r. spectra of **3**, **5**, **8**, and **10** show the expected pattern including a strong peak at about δ 2.4 which must be attributed to the S-methyl group.[8]

Phenyl 1(3)-azulyl sulfides were prepared by the electrophilic substitution of benzenesulfenyl chloride on the azulene, using the general procedure previously employed.[4] Guaiazulene gave 3-phenylthioguaiazulene (**11**), a purple crystalline solid, m.p. 61–62°, when treated with benzenesulfenyl chloride in dry ether at −70°. The reaction of azulene with 1 equiv. of benzenesulfenyl chloride gave results which were originally misleading. A purple crystalline solid, m.p. 75–76°, isolated by chromatography and recrystallization, was thought to be pure 1-phenylthioazulene (**12**). However, closer examination showed that this sample contained a considerable amount of the disubstituted product, 1,3-bis(phenylthio)azulene (**13**). Apparently these two cannot be separated easily by ordinary column chromatography; however, they can be separated by sublimation. Another reaction, in which the benzenesulfenyl chloride was added over a longer period of time and the product was purified by sublimation, afforded **12** in 61% yield as a blue crystal-



12 **13**

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[2] National Science Foundation Undergraduate Research Participant.

[3] A. G. Anderson, Jr., and R. N. McDonald, *J. Am. Chem. Soc.*, **81**, 5669 (1959).

[4] K. Hafner, A. Stephan, and C. Bernhard, *Ann.*, **650**, 42 (1961).

[5] D. S. Matteson and H. R. Snyder, *J. Org. Chem.*, **22**, 1500 (1957).

[6] More recently it was found that this conversion can occur in the absence of the methyl iodide; *cf.* R. K. Olsen and H. R. Snyder, *ibid.*, **30**, 187 (1965).

[7] This compound had previously been prepared by a different method: K. Hafner, H. Patzelt, and H. Kaiser, *Ann.*, **656**, 24 (1962).

[8] The S-methyl resonance of thioanisole occurs at about δ 2.5: N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963, spectrum 490.

line solid, m.p. 83–83.5°. An analytical sample, purified by resublimation, gave material melting at 84–84.5°. The bissulfide **13** was obtained in excellent yield as dark blue needles, m.p. 127–128.5°, when azulene was treated with 2 equiv. of benzenesulfenyl chloride.

Studies on the chemistry of the 1-azulyl sulfides, including their conversion to sulfoxides, sulfones, and sulfonium salts, are in progress.

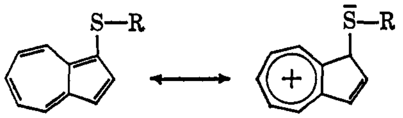
TABLE I

PRINCIPAL VISIBLE ABSORPTION MAXIMA AND SPECTRAL SHIFTS OF 1-AZULYL SULFIDES[a]

Compd.[b]	λ_{max}, mμ	λ_{max}, mμ[c]
1-MeS-Az(**3**)	581	+1
3-MeS-Gz (**5**)	654	+51
1-MeS-TMA (**8**)	589	+42
1,3-diMeS-TMA (**9**)	628	+81
1,3-diMeS-Az (**10**)	627	+47
3-PhS-Gz (**11**)	593	−10
1-PhS-Az (**12**)	570	−10
1-PhS-TMA[d] (**1**)	538	−9
1,3-diPhS-Az (**13**)	578	−2
1,3-diPhS-TMA[d] (**2**)	545	−2

[a] Cyclohexane solution. [b] Az = azulene, TMA = 4,6,8-trimethylazulene, Gz = guaiazulene. [c] Shift measured relative to corresponding hydrocarbon. [d] See ref. 4.

Spectral Shifts.—The spectral shifts of the visible band of azulene due to the alkylthio and arylthio groups have some theoretical significance, and rationalization of these shifts in terms of electronic and steric effects may contribute information to the problems of bonding between divalent sulfur and aromatic systems. The spectral shifts due to the 1(3)-methylthio and 1(3)-phenylthio groups (Table I) are quite interesting since they are inconsistent and violate some well-established empirical rules. All data previously available concerning spectral shifts of the visible band of azulenes showed that the shift due to a particular substituent on a given position was constant and that the spectral shifts were additive[9] for a polysubstituted azulene (unless there were some explicable steric effects). The spectral shifts due to substituents have been interpreted[9-11] in terms of electronic and steric effects. Indeed, these shifts have provided a valuable tool for the investigation and delineation of these effects. Anderson and Steckler[11] have proposed a qualitative interpretation for the spectral shifts due to substituents at the 1- and 3-positions. Their explanation considers the effect of the group in helping to stabilize the ground state, which is electron rich at the 1- and 3-positions, and the excited state, which is electron poor at these positions. It is well known that an electron-donating group in the 1-position causes a bathochromic shift. They have explained this effect as being primarily due to stabilization of the excited state. A 1-alkoxy group has been shown[12] to cause a strong bathochromic shift of about +100 mμ. It is known that a divalent sulfur atom can conjugatively donate electrons, but not as well as an oxygen atom.[13] Thus one would expect a 1(3)-alkylthio group to cause a bathochromic shift also, but of somewhat lesser magnitude than that due to the 1-alkoxy group. The observed shifts of +42 and +51 mμ (Table I) for a 1(3)-methylthio group on 4,6,8-trimethylazulene and guaiazulene, respectively, are therefore not surprising. But the same group on azulene itself effects a negligible shift of +1 mμ. Why should there be such a difference in the spectral shifts caused by a 1(3)-methylthio group on azulene as compared to the alkylazulenes? Since the alkylazulenes have a *peri*-methyl group, it seems likely that there is a steric effect operative, but the exact nature of this effect is unclear. One would expect steric hindrance by the *peri*-methyl group to cause a *lesser* bathochromic shift since it has been shown[14] that electron-releasing conjugation by sulfur, which would stabilize the excited state, is subject to steric effects. It is possible that the *peri*-methyl group hinders electron-accepting resonance by sulfur; such hindrance would cause decreased stability of the ground state with the over-all result being a lower energy of transition. However, this resonance, involving the d orbitals of sulfur, is presumably not very important for divalent sulfur attached to an aromatic ring,[15] and it is not very subject to strict angular requirements.[16]



The spectral shifts caused by the introduction of the second methylthio group in the 3-position further confuse the issue. These shifts should be the same as those due to the original group in the 1-position. However, the second methylthio group on azulene apparently gives a "normal" shift of +46 mμ. The second methylthio group of **9** also causes the expected shift of about +40 mμ. Thus it appears that the spectral shift of **3** is the anomalous one, and a rationalization of this anomaly is not readily apparent.

Since the spectral shift of methyl 1-azulyl sulfide (**3**) is the anomalous one it deserves closer examination, particularly when one notices that the peak at 599 mμ has the same intensity as the one at 581 mμ (which is considered to be the principal absorption maximum). However, one observes that the far wave-length peak of **3** occurs at 692 mμ which is quite close to the wave length, 697 mμ, for the corresponding peak for azulene itself. Therefore the 580-mμ peak (principal absorption maximum) of azulene and the 581-mμ peak of **3** must also correspond.

In contrast to the methylthio group, a 1(3)-phenylthio group effects a shift of −10 mμ whether substituted on azulene, 4,6,8-trimethylazulene, or guaiazulene. The most reasonable explanation for the opposite shifts caused by the two groups is that the phenylthio group is less electron-donating than the methyl-

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[9] E. Heilbronner in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter V.

[10] M. Scholz and W. Treibs, *Z. Elektrochem.*, **65**, 120 (1961).

[11] A. G. Anderson, Jr., and B. M. Steckler, *J. Am. Chem. Soc.*, **81**, 4941 (1959).

[12] L. L. Replogle, *J. Org. Chem.*, **29**, 2805 (1964).

[13] C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, Chapter 2.

[14] E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **71**, 84, 2889 (1949).

[15] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 480.

[16] S. Oae, W. Tagaki, and A. Ohno, *J. Am. Chem. Soc.*, **83**, 5036 (1961).

thio group. An observation which tends to support this assumption is that the carbonyl frequency of compounds of the type RCOSPh is higher (1710 cm.$^{-1}$) than that of its alkyl analog RCOSR (1690 cm.$^{-1}$).[17] Not only would the excited state for phenyl 1-azulyl sulfides be less stabilized by this effect, but the ground state would probably be more stabilized by the greater electron-withdrawing inductive and resonance effects of the 1-SPh group. Electron-withdrawing conjugation of the type proposed earlier might be enhanced by conjugation through sulfur to the phenyl group as shown below. The result of this greater stabilization of the ground state and lesser stabilization of the excited state might be a greater energy of transition and therefore a hypsochromic shift.

More surprising, however, are the spectral shifts caused by the introduction of the second phenylthio group into the 3-position of 1-phenylthio-4,6,8-trimethylazulene and **12**. These compounds show a net hypsochromic shift of −2 mμ from the parent hydrocarbons; thus the second phenylthio group has effected a bathochromic shift of +7–8 mμ. These compounds obviously violate the rule of additivity of spectral shifts, and it is believed that this is the first observation of the reversal of a spectral shift. It is rather difficult to understand these anomalous results, since the 1- and 3-positions of azulene are not directly conjugated with one another, and all previously observed spectra of symmetrically 1,3-disubstituted azulenes have obeyed the additivity rule.

Experimental[18]

The petroleum ether used was reagent grade, b.p. 30–60°. Anhydrous ether was distilled from lithium aluminum hydride just prior to use. Unless otherwise specified, the alumina used for chromatography was Merck acid-washed.

Methyl 1-Azulyl Sulfide (3).—A solution of 91.3 mg. (1.56 mmoles) of potassium hydroxide in a mixture of 2 ml. of methanol and 2 ml. of water was added to a stirred solution of 117 mg. (0.633 mmole) of 1-thiocyanoazulene[3] and 1.0 ml. (16 mmoles) of methyl iodide in 5 ml. of methanol, kept at 0–5° under a nitrogen atmosphere. At the end of 1.5 hr. at ice-bath temperature, the originally purple reaction mixture had become blue. After being stirred at room temperature for an additional 0.5 hr., the reaction mixture was poured into water and extracted with ether. The combined ether extracts were washed with water and saturated salt solution and dried over magnesium sulfate. Removal of solvent left a blue-green oil which was dissolved in a small amount of petroleum ether and chromatographed over acid-washed alumina. Petroleum ether developed a small blue-purple band, which was eluted with that solvent, and a larger blue band, which was eluted with a 3:1 mixture of petroleum ether–carbon tetrachloride. The eluate from the initial band yielded 5 mg. of azulene, while that from the larger blue band yielded 97.4 mg. (88%) of methyl 1-azulyl sulfide (**3**) as a blue-green oil. A cyclohexane solution of **3** showed in the ultraviolet, λ_{max}, mμ (log ε), 200 (4.24), 235 (4.23), 278 (4.46), 285 (4.48), 289 (4.48), 314 (3.86), 344 (3.59), 352 (3.59), and 360 (3.62); and in the visible in mμ (ε), 581 (269), 599 (268), 627 (265), and 695 (141). An n.m.r. spectrum taken in carbon tetrachloride solution showed the S-methyl peak at δ 2.41 and a typical 1-substituted azulene pattern, particularly the doublets (J = 4 c.p.s.) at δ 7.85 and 7.25 corresponding to the 2- and 3-protons, respectively.

Anal. Calcd. for $C_{11}H_{10}S$: C, 75.82; H, 5.78; S, 18.45. Found: C, 75.46; H, 5.82; S, 18.26.

1,3-Bis(methylthio)azulene (10).—Following the same general procedure used for the preparation of **3**, a mixture containing 48 mg. (0.20 mmole) of 1,3-dithiocyanoazulene,[3] 0.5 ml. (8 mmoles) of methyl iodide, 150 mg. of sodium hydroxide, and 7 ml. of methanol was allowed to react at room temperature for 1 hr. After the usual work-up[19] the residue was chromatographed. Petroleum ether developed a blue band followed by a smaller green band. The blue band was eluted with a 4:1 mixture of petroleum ether–dichloromethane and eventually yielded 34 mg. (77%) of 1,3-bis(methylthio)azulene as a green oil. A cyclohexane solution of **10** showed in the ultraviolet, λ_{max}, mμ (log ε), 204 (4.27), 235 (4.27), 283 (4.35), 289 (4.35), 320 (4.03), and 370 (3.69); in the visible region there was a single peak at 627 mμ (ε 279) and a shoulder at 606 mμ (ε 269).

Anal. Calcd. for $C_{12}H_{12}S_2$: C, 65.41; H, 5.49. Found: C, 65.35; H, 5.36.

1-Thiocyano-4,6,8-trimethylazulene (6) and 1,3-Dithiocyano-4,6,8-trimethylazulene (7).—Following the procedure of Anderson and McDonald,[3] a cooled, stirred solution of 1.00 g. (5.89 mmoles) of 4,6,8-trimethylazulene in 30 ml. of dichloromethane under nitrogen was allowed to react with a solution of thiocyanogen [prepared from 1.86 g. (5.76 mmoles) of lead thiocyanate and bromine–carbon tetrachloride solution] in 10 ml. of dichloromethane. After 15 min. at ice-bath temperature, the reaction mixture was allowed to warm to room temperature and stirred for an additional 15 min., during which time it became redder in color. The reaction mixture was washed with sodium bicarbonate solution, then with saturated salt solution, and the solvent was removed. The residue was chromatographed over acid-washed alumina. A 4:1 mixture of petroleum ether–dichloromethane eluted a purple band, from which was recovered 419 mg. of unreacted 4,6,8-trimethylazulene, while a 1:1 mixture of these solvents eluted a red band. Removal of solvent from the red eluate left 570 mg., a 43% (74% net) yield (from azulene) of 1-thiocyano-4,6,8-trimethylazulene, m.p. 126.5–127.5° (lit.[7] 122–123°). An infrared spectrum of a carbon tetrachloride solution of **6** showed a nitrile peak at 4.68 μ; the principal maximum in the visible region for a cyclohexane solution was at 532 mμ (lit.[7] 533 mμ).

The dark red band remaining on the column was eluted with a 4:1 mixture of dichloromethane–ether. The residue from this eluate was rechromatographed; removal of solvent left 212 mg., a 13% (23% net) yield (from azulene), of 1,3-dithiocyano-4,6,8-trimethylazulene as a purple crystalline solid, with some patches of red crystals. Apparently there are two crystalline modifications; the more stable purple form can be obtained as needles, m.p. 154.5–156°, on recrystallization, while the red needles can be obtained by rapid removal of solvent. The two forms are interconvertible in this manner, and on heating, the red form undergoes a transition to the purple form at about 125°.

A chloroform solution of **7** showed in the ultraviolet, λ_{max}, mμ (log ε), 247 (4.45), 308 (4.58), and 346 (3.90); there was a single maximum in the visible at 511 mμ (ε 819).

Anal. Calcd. for $C_{15}H_{12}N_2S_2$: C, 63.34; H, 4.25; N, 9.85. Found: C, 63.42; H, 4.40; N, 9.57.

1-Methylthio-4,6,8-trimethylazulene (8).—Except that no nitrogen atmosphere was employed, the general procedure was that used previously. A mixture containing 340 mg. (1.50 mmoles) of 1-thiocyano-4,6,8-trimethylazulene, 0.60 g. (15 mmoles) of sodium hydroxide, 0.18 ml. (2.3 mmoles) of methyl iodide, and 30 ml. of methanol was allowed to react at room temperature for 0.5 hr. After the usual work-up[19] the residue was chromatographed. Petroleum ether developed a small purple band (eluted with that solvent) followed by a larger blue band; the latter band was eluted with a 4:1 mixture of petroleum ether–dichloromethane and eventually yielded 290 mg. (89%) of 1-methylthio-4,6,8-trimethylazulene as a purple, crystalline solid, m.p. 64–65°. A cyclohexane solution showed in the ultraviolet, λ_{max}, mμ (log ε), 246 (4.44), 302 (4.48), 320 (4.46), 360 (3.70), 372 (3.70), and

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[17] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p. 60.

[18] Melting points were taken on a calibrated Fisher-Johns apparatus. Infrared spectra were recorded using a Beckman IR-5; ultraviolet and visible spectra were taken on a Cary 14. N.m.r. spectra were taken in carbon tetrachloride solution, with tetramethylsilane as the internal marker, using a Varian A-60 spectrometer, and chemical shifts are reported as δ-values. Microanalyses were performed by Dr. A. Bernhardt, Max Planck Institute, Mülheim, Germany, or by Berkeley Analytical Laboratories, Berkeley, Calif.

[19] The usual work-up refers to the treatment of the reaction mixture prior to chromatography as outlined for **3**.

392 (3.67); there was a single broad maximum in the visible at 589 mμ (ϵ 376). Peaks in the n.m.r. spectrum (δ-values) and their assignments are as follows: doublets ($J = 4$ c.p.s.) at 7.38 and 7.12 due to the 2- and 3-protons, respectively; a singlet at 6.68 due to the 5- and 7-protons; S-methyl peak at 2.44; and the ring methyls at 3.22, 2.69, and 2.44. The integrated intensities agree with this assignment.

Anal. Calcd. for $C_{14}H_{16}S$: C, 77.72; H, 7.46. Found: C, 77.65; H, 7.43.

1,3-Bis(methylthio)-4,6,8-trimethylazulene (**9**).—Following the same general procedure, a mixture containing 142 mg. of 1,3-dithiocyano-4,6,8-trimethylazulene, 0.5 ml. (8 mmoles) of methyl iodide, 380 mg. (9.5 mmoles) of sodium hydroxide, and 15 ml. of methanol was stirred at room temperature for 2 hr. during which time it changed from red to blue. After the usual work-up,[19] the green crystalline residue was chromatographed with petroleum ether as the eluent. A large blue band with a small purple front was eluted, leaving a green band behind (eventually eluted with 9:1 petroleum ether–dichloromethane). The crystalline residue from the blue eluate was recrystallized from petroleum ether giving 88.5 mg. (68%) of 1,3-bis(methylthio)-4,6,8-trimethylazulene as green needles, m.p. 97–98°. A cyclohexane solution of **9** showed in the ultraviolet $\lambda_{\max}$, mμ (log ϵ), 206 (4.22), 254 (4.34), 326 (4.34), shoulder at 344 (4.16), and 393 (3.88); there was a single maximum in the visible at 628 mμ (ϵ 403). Peaks in the n.m.r. spectrum (δ-values) and their assignments are: H-2, a singlet at 7.28; H-5 and H-7, a singlet (intensity two) at 6.48; S-methyls at 2.45; 4- and 8-methyls at 3.06; and 6-methyl at 2.36.

Anal. Calcd. for $C_{15}H_{18}S_2$: C, 68.65; H, 6.91. Found: C, 68.83; H, 7.00.

3-Thiocyanoguaiazulene (**4**).—To a stirred solution of 1.00 g. (5.06 mmoles) of guaiazulene in 32 ml. of dry carbon tetrachloride, cooled to 0° and kept under nitrogen, was added thiocyanogen [prepared from 1.80 g. (5.57 mmoles) of lead thiocyanate and an equivalent amount of bromine] in 35 ml. of dry carbon tetrachloride. The reaction mixture, which had become purple, was stirred at 0–5° for 2 hr., transferred to another flask, and stored in the refrigerator for 1 week. The residue left after removal of solvent was dissolved in petroleum ether containing a small amount of carbon tetrachloride and chromatographed over acid-washed alumina. Petroleum ether eluted a dark blue band and a small light blue band, while a 1:24 mixture of carbon tetrachloride–petroleum ether eluted a small yellow-green band. Unreacted guaiazulene (71.5 mg.) was recovered from the first blue eluate. A large purple band was eluted with a 1:3 mixture of dichloromethane–petroleum ether. The residue from the purple eluate was recrystallized from petroleum ether giving 861 mg. (67%) of 3-thiocyanoguaiazulene as short purple rods, m.p. 59–60°. A cyclohexane solution of **4** showed in the ultraviolet, $\lambda_{\max}$, mμ (log ϵ), 245 (4.39), 296 (4.53), 307 (4.42), 357 (3.77), and 375 (3.85); and in the visible in mμ (ϵ) at 578 (484), 616 (41), and 683 (192).

Anal. Calcd. for $C_{16}H_{17}NS$: C, 75.25; H, 6.71; N, 5.48. Found: C, 75.28; H, 6.68; N, 5.65.

3-Methylthioguaiazulene (**5**).—A mixture containing 488 mg. (1.91 mmoles) of 3-thiocyanoguaiazulene, 0.24 ml. (3.8 mmoles) of methyl iodide, 1.1 g. (27 mmoles) of sodium hydroxide, and 20 ml. of methanol was stirred at room temperature under a nitrogen atmosphere for 0.5 hr. After the usual work-up[19] the residue was chromatographed. Petroleum ether developed two blue bands; the small blue band was eluted with that solvent while the larger blue band was eluted with a 5:1 mixture of petroleum ether–dichloromethane. From the first blue eluate was obtained 20 mg. of guaiazulene, while the main blue band yielded 382 mg. (82%) of 3-methylthioguaiazulene as a blue-green oil that slowly crystallized to a green solid, m.p. 54–56°. A cyclohexane solution of **5** showed in the ultraviolet $\lambda_{\max}$, mμ (log ϵ), 249 (3.30), 294 (3.38), 309 (3.33), 373 (3.85), and 392 (3.79); there was a single broad, unsymmetrical peak in the visible region with maximum intensity at 654 mμ (ϵ 353). Peaks in the n.m.r. spectrum (δ-values) and their assignments are: H-8, a weakly split doublet ($J = 2$ c.p.s.) at 7.85; H-3, a singlet at 7.43; H-6, a doublet ($J = 11$ c.p.s.) at 7.11, each peak being further split ($J = 2$ c.p.s.) into a doublet (presumably due to cross-ring coupling with H-8); H-5, a doublet at 6.64; S-methyl at 2.43; ring methyls at 3.14 and 2.57; and isopropyl methyl doublet at 1.31.

Anal. Calcd. for $C_{16}H_{20}S$: C, 78.63; H, 8.25. Found: C, 78.52; H, 8.18.

Phenyl 1-Azulyl Sulfide (**12**).—To a stirred mixture of 257 mg. (2.00 mmoles) of azulene in 20 ml. of anhydrous ether, kept at −40 to −50° under a dry nitrogen atmosphere, was added dropwise 0.23 ml. (290 mg., 2.0 mmoles) of benzenesulfenyl chloride[20] over a period of 30 min. After a period of 20 min. at −40°, the reaction mixture was allowed to warm slowly to room temperature with the temperature held at −30° for 10 min., at −15° for 10 min., and room temperature for another 10 min. The blue reaction mixture was washed with water, and then with 1 *N* sodium hydroxide solution, and dried over sodium sulfate. The residue remaining after removal of solvent was chromatographed over Woelm neutral alumina, and the large blue band was eluted with a 1:1 mixture of petroleum ether–dichloromethane. Sublimation of the crystalline residue from the blue eluate at 75° and 0.1 mm. gave unreacted azulene (22 mg.) as the first fraction. Continued sublimation at *ca.* 0.02 mm. and 75–87° gave phenyl 1-azulyl sulfide (**12**). All fractions collected under these conditions which melted higher than 82° were combined; this amounted to 287 mg. (61%) of a blue, crystalline solid, m.p. 83–83.5°. An additional 57 mg. of less pure (m.p. 78–80°) material was also obtained. An analytical sample, prepared by resublimation, had m.p. 84–84.5°. A cyclohexane solution of **12** showed in the ultraviolet, $\lambda_{\max}$, mμ (log ϵ), 236 (4.46), 281 (4.68), 291 (4.57), 334 (3.73), 343 (3.75), and 359 (3.76); and in the visible in mμ (ϵ), 570 (317), 588 (309), 616 (292), and 675 (128).

Anal. Calcd. for $C_{16}H_{12}S$: C, 81.31; H, 5.12. Found: C, 81.06; H, 5.25.

1,3-Bis(phenylthio)azulene (**13**).—To a cold (−45°), stirred solution of 264 mg. (2.06 mmoles) of azulene in 10 ml. of anhydrous ether was added 0.25 ml. of benzenesulfenyl chloride[20] (nitrogen atmosphere). After a few minutes, another 0.25 ml. of benzenesulfenyl chloride was added (total amount: 630 mg., 4.4 mmoles). After 45 min. at −45°, the mixture was allowed to warm slowly to room temperature and stirred for another 30 min. After concentration, the purple reaction mixture was poured into water, and the suspension was extracted with chloroform. Solvent was removed *in vacuo*, and the residue was recrystallized from cyclohexane–dichloromethane yielding 619 mg. of 1,3-bis(phenylthio)azulene (**13**) as a dark blue, crystalline solid, m.p. 127–128.5°.

Another 30 mg. of **13** was obtained from the mother liquor as dark blue needles, m.p. 128–129.5°. The total yield of **13** was 92%. A cyclohexane solution of **13** showed in the ultraviolet, $\lambda_{\max}$, mμ (log ϵ), 203 (4.69), 237 (4.51), 253 (4.52), 284 (4.52), 295 (4.43), and 361 (3.84); there was a single broad maximum in the visible at 578 mμ (ϵ 346) with a shoulder at 600 mμ (ϵ 340).

Anal. Calcd. for $C_{22}H_{16}S_2$: C, 76.70; H, 4.68. Found: C, 76.73; H, 4.86.

3-Phenylthioguaiazulene (**11**).—Guaiazulene (492 mg., 2.48 mmoles) was allowed to react with 0.28 ml. (350 mg., 2.5 mmoles) of benzenesulfenyl chloride[20] in 5 ml. of anhydrous ether. The reaction mixture, kept under dry nitrogen, was stirred at −70° for 15 min. and then at room temperature for 30 min. The solvent was removed *in vacuo*, leaving a blue oil which was chromatographed; the large blue band was eluted with 1:1 petroleum ether–dichloromethane. Rechromatography using a 4:1 mixture of these solvents as the eluent eventually yielded 627 mg. (82%) of 3-phenylthioguaiazulene as a purple, crystalline solid, m.p. 50–55°. A sample recrystallized from methanol had m.p. 61–62°. A cyclohexane solution of **11** showed in the ultraviolet, $\lambda_{\max}$, mμ (log ϵ), 197 (4.43), 248 (4.52), 294 (4.58), 307 (4.32), 359 (3.89); and in the visible in mμ (ϵ), 593 (477), 639 (410), and 795 (162).

Anal. Calcd. for $C_{21}H_{22}S$: C, 82.29; H, 7.24. Found: C, 82.32; H, 7.22.

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(20) H. Lecher and F. Holschneider, *Ber.*, **57**, 755 (1924).