Some Chemistry and Crystallography of the Heptafulvenothiophene–Azulenodihydrothiophene System

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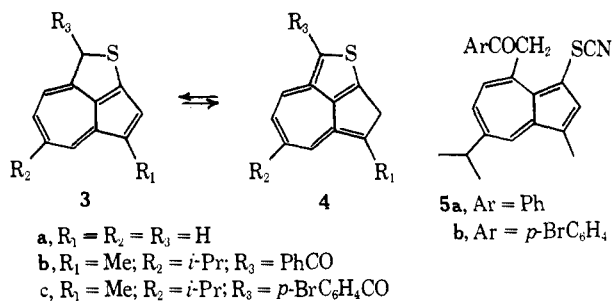
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Abstract: The synthesis of 2H-azuleno[1,8-bc]thiophene and 2-benzoyl-8H-azuleno[1,8-bc]thiophene derivatives has shown that the azulenodihydrothiophene system is thermodynamically more stable than the heptafulvenothiophene tautomer, but that substitution of a strong conjugating group in the 2 position reverses the stability order. The details of several HMO calculations, which lend support to these data, are reported. The crystal and molecular structure of 2-(p-bromobenzoyl)-5-isopropyl-7-methyl-8H-azuleno[1,8-bc]thiophene has been determined by three-dimensional, X-ray diffraction analysis. The material crystallizes in the monoclinic system with unit cell parameters of $a = 9.063$, $b = 10.807$, $c = 19.368$ Å, $\beta = 102.38°$. All of the atoms have been located and refined with full-matrix least squares to a final R index of 0.049. The thiophene ring bond lengths show the influence of conjugation with the benzoyl substituent and these data have been correlated with HMO π-bond orders.

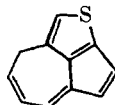Some recent studies[2,3] on the azulenocyclohexadiene (1)–benzoheptafulvene (2) system have established that the benzenoid tautomer 2 is thermodynamically
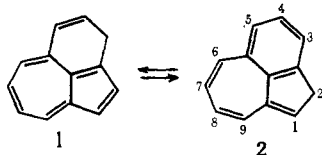
more stable than the azulenoid tautomer 1. These experimental observations are consistent with the relative order of stability suggested by HMO calculations[4] of π-electron delocalization energies. Substitution of a sulfur atom for the C(3)–C(4) ethylenic linkage in 2 forms a new heterocyclic molecule which can exist in several tautomeric forms (e.g., 3 and 4) similar to those indicated for 1 and 2. In this case, however, the stability of an azulene 3 vs. that of a thiophene 4 must be

considered, and, in view of the lower resonance energy of thiophene compared to benzene, structure 3 might be expected to be the more stable of the two. Delocalization energies calculated for these two sulfur heterocycles have predicted greater π-electron stability in 3a than 4a.[4] However, the recent synthesis of a benzoyl-dialkyl derivative by treatment of the thiocyano ketone 5a with base, a method which should permit isolation of the most stable isomer, 3b or 4b, has shown that the benzoylheptafulvenothiophene tautomer (4b) predominates.[5]

Further data bearing on the question of relative tautomeric stabilities in this heterocyclic system are presented and discussed in this paper.

Experimental Section

Melting points were taken on a Fisher–Johns apparatus and are uncorrected. Infrared spectra were recorded using a Beckman IR-5; ultraviolet and visible spectra were taken on a Cary 14. Nuclear magnetic resonance spectra were taken on a Varian A-60 spectrometer except for the dimer 10 which was taken on an HA-100, with tetramethylsilane as the internal marker. Coupling constants were taken directly from the spectra and are apparent values. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich., or by Berkeley Analytical Laboratories, Berkeley, Calif. Mass spectra were obtained on Hitachi Perkin-Elmer Model RMU-6E or CEC 21-491 instruments.

7-Isopropyl-1-methyl-4-p-bromophenacylazulene. This ketone was prepared from 1.98 g (10.0 mmol) of guaiazulene, 16.4 ml of a 0.641 N ethereal solution of sodium N-methylanilide (10.5 mmol), and 1.82 g (10.0 mmol) of p-bromobenzonitrile using the method[6] previously employed for 7-isopropyl-1-methyl-4-phenacylguaiazulene. The product was recrystallized from Skellysolve B giving 2.18 g (58%) of the ketone as blue crystals: mp 132–132.5°; uv λ_{max} (cyclohexane) 254 (log ϵ 4.63), 287 (4.63), 290 (4.62), and 353 nm (3.66); vis λ_{max} (cyclohexane) 610 (log ϵ 2.72), shoulder at 631 (2.69), 664 (2.66), and 740 nm (2.33); ir (CCl₄) 5.95 μ (C=O); nmr (CDCl₃) τ 2.44 (d, 1, $J = 3.5$ Hz, H-2), 2.80 (d, 1, $J = 3.5$ Hz, H-3), 3.07 (d, 1, $J = 10$ Hz, H-5), 2.57 (dd, 1, $J = 10$, 1.5 Hz, H-6), 1.77 (d, 1, $J = 1.5$ Hz, H-8), 2.0–2.6 (m, 4, phenyl), 5.32 (s, 2, CH₂), 7.35 (s, 3, 1-Me), 6.93 (m, 1, $J = 7$ Hz, CH of i-Pr), and 8.67 (d, 6, $J = 7$ Hz, Me of i-Pr).

7-Isopropyl-1-methyl-3-thiocyano-4-p-bromophenacylazulene (5b). Thiocyanogen generated from 1.292 g (4.0 mmol) of lead thiocyanate and 20% bromine in carbon tetrachloride solution was allowed to react with 1.524 g (3.88 mmol) of the above ketone

a, R₁ = R₂ = R₃ = H
b, R₁ = Me; R₂ = i-Pr; R₃ = PhCO
c, R₁ = Me; R₂ = i-Pr; R₃ = p-BrC₆H₄CO

5a, Ar = Ph
b, Ar = p-BrC₆H₄

(1) (a) University of Maryland; (b) San Jose State College.

(2) K. Hafner and H. Schaum, *Angew. Chem., Int. Ed. Engl.*, 2, 95 (1963).

(3) V. Boekelheide and C. D. Smith, *J. Amer. Chem. Soc.*, 88, 3950 (1966).

(4) (a) There are several possible positions for the tautomeric hydrogen atom in the thiophene derivative, of which structure 4 is one example. In terms of ω-HMO[4b] π-electron stability calculations, the delocalization energy of the structure shown below (3.38 β) is slightly larger than that computed for 4a (3.34 β). (b) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 135.

(5) L. L. Replogle, K. Katsumoto, and H. L. Ammon, *J. Amer. Chem. Soc.*, 90, 1086 (1968).

in carbon tetrachloride solution kept at $-10°$.[6,7] The product was recrystallized from Skellysolve B giving 760 mg (43%) of **5b** as dark purple crystals: mp 135–137°; uv λ_{max} (cyclohexane) 261 (log ϵ 4.64), 297 (4.58), shoulder at 351 (3.68), 366 (3.76), and 377 nm (3.86); vis λ_{max} (cyclohexane) 584 (log ϵ 2.80), and shoulders at 622 (2.75) and 690 nm (2.34); ir (CHCl₃) 5.91 (C=O) and 4.65 μ (S—C≡N); nmr (CDCl₃) τ 2.25 (s, 1, H-2), 2.90 (d, 1, $J = 10$, Hz, H-5), 2.43 (dd, 1, $J = 10$, 1.5 Hz, H-6), 1.70 (d, 1, $J = 1.5$ Hz, H-8), 2.02–2.5 (m, 4, phenyl), 4.73 (s, 2, CH₂), 7.42 (s, 3, 1-Me), 6.87 (m, 1, $J = 7$ Hz, CH of i-Pr), and 8.63 (d, 6, $J = 7$ Hz, Me of i-Pr).

Anal. Calcd for C₂₃H₂₀BrNOS: C, 63.01; H, 4.60; N, 3.20; S, 7.32. Found: C, 62.88; H, 4.79; N, 3.03; S, 7.10.

1,4,6-Trimethyl-2H-azuleno[1,8-bc]thiophenium Tetrafluoroborate (7). Hydrogen chloride gas was passed over a cooled (5°), stirred solution of 100 mg (0.043 mmol) of an approximately 2:1 mixture of 6,8-dimethyl-4-methylsulfinylmethylazulene (6) and its isomer 4,8-dimethyl-6-methylsulfinylmethylazulene in 10 ml of acetonitrile until tlc (silica gel, petroleum ether–dichloromethane) indicated maximum yield of cyclic sulfonium salt (immobile red spot at the origin). The reaction time was *ca.* 5 min. Solvent and excess hydrogen chloride were removed *in vacuo* and the residue was dissolved in a small amount of dichloromethane. This solution was extracted with water giving a red aqueous extract and a brown organic phase. An aqueous solution of 0.93 mg (0.48 mmol) of silver tetrafluoroborate was added to the water phase and the resulting precipitate of silver chloride was removed by filtration. The red solution was concentrated by boiling to a small volume, and this was extracted with several large portions of dichloromethane. The combined dichloromethane extracts were dried (Na₂SO₄) and the solvent was removed *in vacuo*. Recrystallization of the residue from petroleum ether–dichloromethane gave 28 mg of **7** as red crystals: mp 161.5–164°; uv λ_{max} (CHCl₃) 283 (log ϵ 4.49), shoulder at 294 (4.49), 303 (4.59), 332 (3.78), 342 (3.82), and 348 nm (3.86); vis λ_{max} (CHCl₃) at 533 (log ϵ 2.92) and shoulder at 640 nm (2.27); nmr (CF₃CO₂H) τ 2.15 (d, 1, $J = 4$ Hz, H-8), *ca.* 2.4 (m, 3, H-3, H-5, H-7), 5.55 and 5.98 (pair of doublets, 2, $J = 17$ Hz, nonequivalent CH₂ protons), 6.88 (s, 3, 1-Me), 7.02 (s, 3, 6-Me), and 7.15 (s, 3, 4-Me).

Anal. Calcd for C₁₄H₁₅BF₄S: C, 55.62; H, 5.01; S, 10.62. Found: C, 55.39; H, 4.99; S, 10.36.

A second crop of crystals (7 mg, mp 158–161°) was collected giving a total yield of 25%.

4,6-Dimethyl-2H-azuleno[1,8-bc]thiophene (8). A mixture of 20 mg of 1,4,6-trimethyl-2H-azuleno[1,8-bc]thiophenium tetrafluoroborate (7), 1 ml of pyridine, 500 mg of sodium iodide, and *ca.* 30 ml of acetone was stirred at room temperature. After 15 min, tlc (silica gel, petroleum ether) indicated that the reaction was complete, and the mixture was poured into an ether–water mixture. The blue ether layer was washed with water and dried (Na₂SO₄) and the solvent was removed with a rotary evaporator. Chromatography of the residue on silica gel (Silicar CC-7) using petroleum ether as the eluent gave a single blue band from which the sulfate **8** was isolated as dark blue-green plates in essentially quantitative yield: mp 111.5–113.2° (analytical sample had mp 115.5–116.5°); uv λ_{max} (cyclohexane) 238 (log ϵ 4.25), 308 (4.29), 322 (4.38), 369 (3.44), 387 (3.69), 402 (3.76), and 408 nm (394); vis λ_{max} (cyclohexane) shoulder at 600 (log ϵ 2.51), 647 (2.64), 692 (2.62), 716 (2.60), 773 (2.30), and 809 nm (2.21); nmr (CDCl₃) τ 3.08 (s. 2, H-2 and H-3), 3.60 (s, 1, H-5 or H-7), 3.74 (s, 1, H-7 or H-5), 5.16 (s, 2. CH₂), 7.54 (s, 3, 4-Me), and 7.67 (s, 3, 6-Me); mass spectrum (70 eV) m/e (relative intensity) 202 (10), 201 (12), 200 (M⁺, 100), 199 (34), 186 (9), 185 (64), 184 (20), 152 (10).

Anal. Calcd for C₁₃H₁₂S: C, 77.95; H, 6.04; S, 16.01. Found: C, 77.94; H, 5.99; S, 16.09.

There was no change in the visible or near-ultraviolet (300–410 nm) spectrum of **8** when a 3-ml portion of a solution, made from 5.4 mg of the material and 10 ml of methanol, was treated with 10 μl of 0.56 N sodium hydroxide.

2-Benzoyl-5-isopropyl-7-methyl-8H-azuleno[1,8-bc]thiophene (4b). Argon was bubbled through a solution containing 121 mg (0.337 mmol) of 7-isopropyl-1-methyl-4-phenacyl-3-thiocyanoazulene (5a), 5 ml of ether, and 8 ml of methanol; then 1.0 ml of 0.55 M methanolic potassium hydroxide in 3 ml of methanol was added over a period of 5 min to the stirred solution. The solution, which had

become bright red, was stirred for an additional 5 min and 5 ml of 0.12 N hydrochloric acid was added. This mixture was extracted with ether; the ether extract was washed well with water and dried. Removal of solvent left a red solid which was chromatographed over Mallinckrodt Silicar CC-7 silica gel. The large red band was eluted with 2:1 petroleum ether–dichloromethane. Removal of solvent from the red eluate left 101 mg (90%) of the heterocycle **4b** as a red, crystalline solid, mp 106–109°.

A similar reaction using the same quantity of **5a**, 0.5 ml of pyridine, and dimethyl sulfoxide (5 ml) as the solvent and a reaction time of 6 hr afforded **4b** in 82% yield (mp 105–109°). This product was recrystallized from hexane to give a 69% yield: mp 109.5–111°; uv λ_{max} (CHCl₃) 263 (log ϵ 4.26) and 348 nm (4.21); vis λ_{max} (CHCl₃) 504 nm (log ϵ 3.08); ir (CCl₄) 6.11 μ (C=O); nmr (CDCl₃) τ 2.25 (m, 2, o-H), 2.53 (m, 3, m and p-H), 3.28 (d, 1, $J = 12$ Hz, H-3), 4.40 (d, 1, $J = 12$ Hz, H-4), 3.93 (s, 1, H-6), 6.78 (s, 2, CH₂), 8.07 (s, 3, 7-Me), and 8.97 (d, 6, $J = 7$ Hz, Me of i-Pr). A precise mass spectral measurement gave a molecular weight of 332.12 (relative intensity 100); other prominent peaks were observed at m/e (relative intensity) 334 (17), 333 (46), 331 (8), 318 (11), 317 (39), 290 (10), 289 (46), 274 (8), 261 (13), 227 (34), 212 (13), 211 (13), 197 (8), 152 (8), 105 (49), and 77 (30).

Anal. Calcd for C₂₂H₂₀OS: C, 79.48; H, 6.06; S, 9.65. Found: C, 79.52; H, 5.96; S, 9.37.

2-(p-Bromobenzoyl)-5-isopropyl-7-methyl-8H-azuleno[1,8-bc]-thiophene (4c). Argon was bubbled through a solution of 110 mg (0.25 mmol) of the p-bromo ketone **5b** in 6 ml of dimethyl sulfoxide and 0.5 ml (6 mmol) of pyridine. After 1.25 hr, the solution was filtered and shiny red crystals were collected. The filtrate was extracted with ether, and this ether extract was washed with dilute hydrochloric acid and water and then dried. The residue was chromatographed over Silicar CC-7 silica gel and the reddish purple band was eluted with 4:1 carbon tetrachloride–ether. The residue from the red eluate was combined with the red crystals collected by filtration. This mixture was recrystallized from ligroin giving 48 mg of red, sword-like crystals, mp 158–160°. A second crop, consisting of 21 mg, mp 154–156°, was also collected. The combined yield was 67%. Compound **4c** had the following spectral data: uv λ_{max} (CHCl₃) 268 (log ϵ 4.31) and 350 nm (4.23); vis λ_{max} (CHCl₃) 511 nm (log ϵ 3.08); ir (neat) 6.15 μ (C=O); nmr (CDCl₃) τ 2.40 (broad singlet, 4, phenyl), 3.32 (d, 1, $J = 12$ Hz, H-3), 4.37 (d, 1, $J = 12$ Hz, H-4), 3.92 (s, 1, H-6), 6.77 (s, 2, CH₂), 8.02 (s, 3, 7-Me), and 8.95 (d, 6, $J = 7$ Hz, Me of i-Pr).

Anal. Calcd for C₂₂H₁₉OSBr: C, 64.23; H, 4.66; Br, 19.43. Found: C, 63.85; H, 4.93; Br, 19.58.

Dimer 10. A. From Thiocyano Ketone 5a. To a stirred solution of 121 mg (0.337 mmol) of the thiocyano ketone **5a** in 8 ml of methanol and 5 ml of ether was added a solution of 1.0 ml of 0.55 M methanolic potassium hydroxide in 3 ml of methanol over a period of 5 min. The mixture was stirred for another 5 min and then filtered to collect the red solid. This solid was recrystallized from carbon tetrachloride yielding 70 mg (63%) of the dimer **10**: mp 215–215.5° dec (sealed, evacuated capillary); uv λ_{max} (CHCl₃) 262 (log ϵ 4.24) and 349 nm (4.15); vis λ_{max} (CHCl₃) 495 nm (log ϵ 3.01); ir (Nujol) 6.16 μ (C=O); nmr τ 2.33 (m, 2, o-H), 2.62 (m, 3, m- and p-H), 3.21 (d, 1, $J = 12.5$ Hz, H-3), 3.89 (s, 1, H-6), 4.24 (d, 1, $J = 12.5$ Hz, H-4), 6.23 (s, 1, methine H), 7.97 (s, 3, 7-Me), and 8.90 (d, 6, $J = 7$ Hz, Me of i-Pr).

Anal. Calcd for C₄₄H₃₈O₂S₂: C, 79.72; H, 5.78; S, 9.67. Found: C, 79.32; H, 5.91; S, 9.82.

B. From Monomer 4b. To a stirred mixture of 33 mg of **4b** in a mixture of 4 ml each of methanol and ether was added 0.010 ml of 0.55 N methanolic potassium hydroxide. The mixture darkened and a red solid precipitated. Filtration afforded 21 mg (64%) of the dimer.

A very low yield of the dimer was obtained from a similar experiment using an inert (Ar) atmosphere.

Preliminary X-Ray Crystallographic Study of Compound 10. The material recrystallized from chloroform as dark red rhombs. Oscillation and Weissenberg X-ray photographs of a specimen mounted parallel to one of the crystal diagonals established the crystal system as monoclinic and an analysis of the systematic absences gave the space group $B2_1/a$. This space group was transformed to $P2_1/n$ with unit cell parameters of $a = 13.24$, $b = 13.08$, $c = 22.29$ Å, $\beta = 113.5°$. A crystal density of 1.249 g cm⁻³ was measured by the neutral buoyancy method in a cyclohexane–*sym*-tetrabromoethane solvent mixture. Mol wt calcd for (C₂₂H₁₉SO)₂: 662.8. Found: 665.8 for four molecules per unit cell. Calcd for C₂₂H₂₀SO: 332.4. Found: 332.9 for eight molecules per unit cell.

(6) L. L. Replogle, K. Katsumoto, T. C. Morrill, and C. A. Minor, *J. Org. Chem.*, 33, 823 (1968).

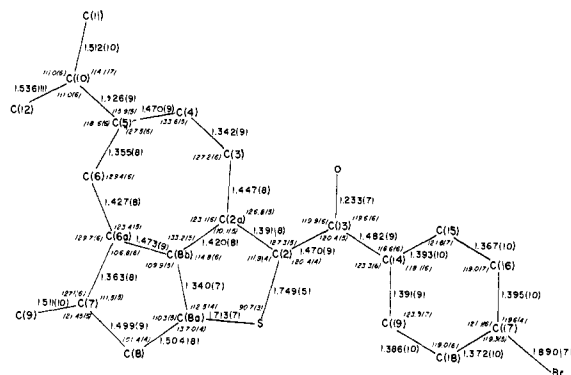(7) A. G. Anderson, Jr., and R. N. McDonald, *J. Amer. Chem. Soc.*, 81, 5669 (1959).

Figure 1. Bond lengths (ångströms) and angles (degrees) between the C, O, S, and Br atoms in 2-(p-bromobenzoyl)-5-isopropyl-7-methyl-8H-azuleno[1,8-bc]thiophene. Estimated standard deviations are given in parentheses.

X-Ray Crystallographic Investigation of 2-(p-Bromobenzoyl)-5-isopropyl-7-methyl-8H-azuleno[1,8-bc]thiophene (4c).

Compound **5b** recrystallized from methanol as red-purple needles. Oscillation, Weissenberg, and precession photographs established the crystal system as monoclinic and the needle axis as *b*. The diffraction maxima were first recorded on equiinclination Weissenberg films using Cu radiation for the *h*0*l*–*h*9*l* and *hk*0–*hk*2 levels and the intensities were measured with a Joyce-Deeley flying spot microdensitometer. These film data were used to solve the structure and in the first cycles of least-squares refinement, but the final calculations were made using a set of diffractometer data collected at a later time. The diffractometer measurements were made using Nb-filtered Mo radiation and a Datex automated, General-Electric instrument equipped with a quarter-circle goniostat. A crystal of **5b** mounted parallel to *b*, *ca.* 0.4-mm long and 0.1 × 0.2 mm in cross section, was used for all cell parameter and intensity determinations. The lattice parameters were obtained by the least-squares refinement of 13 carefully measured Bragg angles. The crystal density was determined by the neutral buoyancy method in aqueous potassium iodide solution. The crystal data are: molecular formula, $C_{22}H_{19}BrSO$, mol wt 411.4; X radiation, Mo Kα, $\lambda = 0.71069$ Å; monoclinic unit cell parameters, $a = 9.063 \pm 0.003$, $b = 10.807 \pm 0.002$, $c = 19.368 \pm 0.009$ Å, $\beta = 102.38 \pm 0.03°$; measured density, 1.470 g cm^{-3}; calculated density, 1.474 g cm^{-3} for four molecules/unit cell; unit cell volume, 1852 Å^3; $F(000)$, 840 e; linear absorption coefficient, 24.1 cm^{-1}; absent spectra, *h*0*l* for *h* + *l* odd and 0*k*0 for *k* odd; space group, $P2_1/n$.

The intensity measurements were made using the 2θ scan technique with two 10-sec background measurements. The scan speed was 2° min^{-1} and the scan ranges were predetermined using the tan θ function of Alexander and Smith.[8] Of the 5386 unique reflections measured out to sin θ/λ of 0.7035 ($2\theta = 60°$), 2054 (38.1%) of the intensities were more than three standard deviations above background and were coded "observed." The remaining data were called "unobserved" and assigned intensities equal to 3σ. The intensities of five standard reflections, measured at 1–2-hr intervals to monitor intensity fluctuations, showed a monotonic decrease during the data collection and an overall intensity decrease of *ca.* 4% from beginning to end. A total of 6229 data and 106 standard groups was measured using the one crystal. The intensity sum of each standard reflection group was expressed as a function of the total number of data measured up to that point, which was an approximation to the amount of X-ray exposure received by the sample, and a least-squares lines was fit to these data using the computer program DATA.[9] The scaling algorithm was developed in a way that assigned factors of 0.98, 1.0, and 1.02 to the first, middlemost, and last reflections measured. The standard deviation of the line was 0.005 ($\sigma = [\Sigma_{i=1}^{106}(K_{o,i} - K_{c,i})^2/(106 - 1)]^{1/2}$, where K_i is the scale factor of the *i*th standard reflection group).

The structure was solved using the film data. The intensities were reduced in the normal way, and scale, temperature, and normalized structure factor amplitudes ($|E|$'s) were computed with

the X-ray 63 subprogram DATFIX.[10] Two plausible locations for the Br atom, both of which had *y* coordinates of 0.25, were found from the sharpened, origin-free Patterson synthesis calculated using $E^2 - 1$ for the Fourier coefficients. Subsequent electron density maps computed with the Br phases contained false mirror planes at *y* = 0.25 and 0.75, features which complicated the search for remaining atoms. Although this path would have led eventually to a solution, we thought that the symbolic addition procedure[11] offered a less expensive way to proceed in terms of computer time. Following some preliminary work with the X-ray 63 subprogram SIGMA2, it was determined that a large-phase pyramid could be constructed starting with the phases of three origin-fixing reflections (4, 3, 0; 1, 2, −3; 1, 4, −6) and one unknown reflection (3, 7, −10). Phases were determined for 268 reflections from a starting set of 302 data which contained all *E*'s greater than 1.6. The two possible phases for 3, 7, −10 generated two sign pyramids, but the two solutions were different by only 19 phases and thus were considered to be identical. An *E* map calculated with these 268 terms clearly revealed the positions of the bromine and 19 of the carbon atoms, a subsequent structure factor calculation gave an *R* index[12] of 0.50, and the remaining atoms were readily located from an electron-density synthesis.

Full-matrix least-squares refinement, which initially used the film data and isotropic temperature factors, was completed using the diffractometer measurements and anisotropic temperature factors for all atoms except hydrogen. The hydrogen atoms were located from a difference synthesis and included with individual isotropic temperature factors. The quantity minimized by least squares was $\Sigma w(|F_o| - k|F_c|)^2$, with the weights (*w*'s) calculated from $w^{1/2} = 3.0/\text{MAX}[\sigma(F_o), 0.21|F_o| + 3.0]$.[13] The unobserved data were included in the refinement in the following way: $w = 0$ if $|F_c| < |F_o|$ and $w = 1/\sigma^2(F_o)$ if $|F_c| > |F_o|$. The refinement was continued until all parameter shifts were less than 0.1 standard deviation and the final *R* and weighted R^{14} indices were 0.049 and 0.056, respectively. In the final cycle of refinement, 323 of the 3332 unobserved data showed $|F_c|$'s which were larger than the corresponding $|F_o|$'s. The atomic form factors used in this investigation were taken from the following sources: carbon and oxygen, Berghius, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal;[15] sulfur and bromine, "International Tables for X-ray Crystallography";[16] hydrogen, Stewart, Davidson, and Simpson.[17]

Atomic coordinates and thermal parameters are given in Table I. Bond lengths and angles for the C, O, S, and Br atoms are shown in Figure 1 and lengths and angles to hydrogen are listed in Table II. A copy of the structure factor data has been deposited with ASIS–NAPS.[18]

Discussion

It is proposed in an initial communication[5] that the 2-benzoyl substituent was probably responsible for the

(8) L. E. Alexander and G. S. Smith, *Acta Crystallogr.*, 17, 1195 (1964).

(9) H. L. Ammon, "DATA, A Program for the Scaling of Counter Data," 1967, unpublished.

(10) The majority of the computations were done with the X-ray 63 and X-ray 67 crystallographic program systems on the University of Maryland IBM 7094 and UNIVAC 1108 machines; X-ray 63, Crystal Structure Calculations System, Technical Report 64-6 (NSG-398), Computer Science Center, University of Maryland, and Research Computer Laboratory, University of Washington, 1964; X-ray 67, Program System for X-ray Crystallography, Technical Report 67-58 (NSG-398), Computer Science Center, University of Maryland, 1967.

(11) J. Karle and I. L. Karle, *Acta Crystallogr.*, 21, 849 (1966).

(12) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

(13) MAX refers to the Fortran maximum value function. The standard deviations were determined from counting statistics. This function served to reduce the importance of the strongest and weakest data in the refinement. A final analysis of the weighting scheme showed no trend in the quantity $w(|F_o| - |F_c|)^2$ with either sin θ/λ or $|F_o|$.

(14) Weighted $R = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

(15) J. Berghius, I.-J. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Crystallogr.*, 8, 478 (1955).

(16) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(17) R. F. Stewart, E. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(18) A table of observed and calculated structure factor amplitudes has been deposited as Document No. NAPS-01141 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and remitting $6.80 for photocopies or $2.00 for microfiche. Advance payment is required. Make checks or money orders payable to CCMIC-NAPS.

Table I. Fractional Atomic Coordinates and Temperature Parameters (Å^2)[a]

Atom	x	y	z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	0.30032 (9)	0.74101 (8)	0.26156 (4)	4.85 (4)	4.71 (4)	5.12 (4)	−0.64 (3)	0.82 (3)	1.36 (3)
S	0.0178 (2)	0.2973 (2)	0.4460 (1)	2.52 (6)	3.6 (1)	3.3 (1)	0.4 (1)	0.6 (1)	0.4 (1)
O	0.4565 (5)	0.2870 (4)	0.5097 (2)	2.6 (2)	4.6 (3)	5.5 (2)	0.5 (2)	1.2 (2)	1.4 (2)
C(2)	0.1953 (6)	0.2770 (5)	0.5019 (3)	2.2 (2)	2.7 (3)	3.2 (2)	−0.1 (2)	0.7 (2)	−0.1 (2)
C(2a)	0.1891 (6)	0.1967 (6)	0.5574 (3)	2.1 (2)	2.8 (2)	3.3 (2)	0.3 (2)	0.7 (2)	−0.6 (2)
C(3)	0.3132 (7)	0.1616 (6)	0.6142 (3)	2.5 (2)	3.3 (3)	3.7 (3)	−0.3 (2)	0.7 (2)	0.1 (2)
C(4)	0.3098 (6)	0.0807 (6)	0.6664 (3)	2.3 (2)	3.4 (3)	3.6 (2)	−0.2 (2)	−0.1 (2)	0.1 (2)
C(5)	0.1919 (7)	−0.0002 (5)	0.6832 (3)	3.1 (3)	2.1 (3)	3.1 (3)	−0.1 (2)	0.7 (2)	−0.1 (2)
C(6)	0.0432 (7)	−0.0019 (6)	0.6516 (3)	2.4 (2)	3.1 (3)	3.2 (3)	−0.2 (2)	0.8 (2)	−0.4 (2)
C(6a)	−0.0360 (6)	0.0683 (5)	0.5928 (3)	2.3 (3)	2.8 (3)	2.7 (2)	0.1 (2)	0.7 (2)	−0.8 (2)
C(7)	−0.1852 (6)	0.0662 (6)	0.5604 (3)	2.3 (2)	3.0 (3)	3.7 (3)	0.1 (2)	0.8 (2)	−0.7 (2)
C(8)	−0.2163 (6)	0.1463 (6)	0.4957 (3)	2.2 (2)	3.7 (3)	3.9 (3)	0.3 (2)	0.2 (2)	−0.9 (2)
C(8a)	−0.0619 (6)	0.1984 (6)	0.4968 (3)	2.3 (2)	3.0 (3)	3.3 (3)	0.2 (2)	0.9 (2)	−0.2 (2)
C(8b)	0.0390 (6)	0.1538 (6)	0.5521 (3)	2.3 (2)	3.1 (2)	2.4 (2)	0.4 (2)	0.6 (2)	−0.6 (2)
C(9)	−0.3098 (7)	−0.0054 (7)	0.5832 (4)	2.9 (3)	4.2 (3)	5.5 (4)	−0.3 (2)	1.4 (3)	0.1 (3)
C(10)	0.2497 (7)	−0.0921 (6)	0.7427 (4)	3.1 (2)	3.5 (3)	4.2 (3)	−0.1 (2)	0.7 (2)	0.3 (2)
C(11)	0.3184 (9)	−0.0323 (8)	0.8128 (4)	4.9 (4)	6.1 (4)	3.7 (4)	−0.3 (3)	0.2 (3)	0.6 (3)
C(12)	0.3595 (9)	−0.1853 (7)	0.7210 (4)	4.8 (4)	4.7 (4)	7.0 (5)	1.6 (3)	1.2 (3)	1.6 (4)
C(13)	0.3310 (7)	0.3298 (6)	0.4832 (3)	2.6 (2)	3.0 (3)	3.6 (3)	0.1 (2)	0.6 (2)	−0.1 (2)
C(14)	0.3174 (7)	0.4294 (6)	0.4296 (3)	2.6 (2)	3.2 (3)	3.4 (3)	0.1 (2)	1.1 (2)	−0.5 (2)
C(15)	0.4104 (8)	0.4252 (7)	0.3810 (4)	4.1 (3)	4.2 (3)	4.4 (3)	0.7 (3)	1.8 (3)	−0.1 (3)
C(16)	0.4049 (8)	0.5148 (7)	0.3307 (4)	4.0 (3)	5.0 (4)	4.2 (3)	0.5 (3)	2.2 (3)	0.5 (3)
C(17)	0.3065 (7)	0.6144 (6)	0.3295 (3)	3.6 (3)	4.0 (3)	3.4 (3)	0.6 (3)	0.7 (2)	0.3 (2)
C(18)	0.2164 (7)	0.6237 (6)	0.3779 (4)	3.4 (3)	3.2 (3)	4.2 (3)	−0.2 (2)	1.0 (2)	−0.3 (2)
C(19)	0.2207 (7)	0.5301 (6)	0.4272 (4)	3.5 (3)	3.4 (3)	4.2 (3)	.0.2 (2)	1.9 (2)	−0.6 (2)
H(3)	0.408 (7)	0.221 (7)	0.619 (3)	6 (1)					
H(4)	0.403 (6)	0.075 (5)	0.703 (3)	4 (1)					
H(6)	−0.021 (6)	0.061 (5)	0.667 (3)	3 (1)					
H(8a)	−0.280 (7)	0.204 (6)	0.497 (3)	5 (1)					
H(8b)	−0.253 (5)	0.099 (5)	0.458 (3)	2 (1)					
H(9a)	−0.274 (7)	−0.063 (6)	0.625 (3)	6 (1)					
H(9b)	−0.361 (7)	−0.042 (6)	0.542 (3)	5 (2)					
H(9c)	−0.365 (10)	0.055 (9)	0.595 (5)	10 (2)					
H(10)	0.162 (5)	−0.137 (5)	0.747 (3)	2 (3)					
H(11a)	1.255 (8)	1.027 (7)	0.825 (4)	6 (2)					
H(11b)	1.400 (9)	1.019 (8)	0.807 (4)	8 (2)					
H(11c)	1.341 (9)	1.908 (8)	0.855 (4)	8 (2)					
H(12a)	0.301 (9)	−0.219 (7)	0.666 (4)	8 (1)					
H(12b)	0.445 (9)	−0.144 (7)	0.711 (4)	7 (2)					
H(12c)	0.393 (8)	−0.232 (8)	0.755 (4)	8 (2)					
H(15)	0.462 (7)	0.348 (6)	0.380 (3)	5 (2)					
H(16)	0.451 (7)	0.503 (6)	0.296 (2)	6 (2)					
H(18)	0.148 (6)	0.699 (5)	0.379 (3)	4 (2)					
H(20)	0.170 (6)	0.533 (5)	0.462 (3)	3 (1)					

[a] Estimated standard deviations are given in parentheses. The anisotropic temperature factors in the form $\exp[-0.25(B_{11}h^2a^{*2} + \ldots 2B_{23}klb^*c^*)]$.

greater stability of the heptafulvenothiophene **4b** over that of the azulenodihydrothiophene tautomer **3b** since the benzoyl group is conjugated with the π system in **4b** but not in **3b**. More recent data have confirmed this supposition.

To explore this problem fully, we have made a series of ω-HMO calculations[19] on various formyl- and benzoylthiophenes and on the heptafulvenothiophene π-electron system. Sulfur was handled according to the split atom technique of Longuet-Higgins[20] and the oxygen coulomb integral was equated to $\alpha_c + 1.0\beta$.[4b] Wherever appropriate the thiophene–carbonyl and benzene–carbonyl bond integrals used were corrected for the C(2)–C(13) and C(13)–C(14) dihedral angles[21] observed in the crystal structure of **4c** (see below). The π-electron delocalization energies computed for several of the compounds are given in Table III.

Although the calculations indicate greater π stability in **3a** relative to **4a**, inclusion of the benzoyl substituent in these calculations reverses the order making **4b**

more stable than **3b**. Linking the benzoyl and heptafulvenothiophene groups gives a molecule (**4b**) whose delocalization energy is *ca.* 0.4β greater than the sum of the delocalization energies of the separate pieces. The influence of the benzoyl substituent on the stability of **4b** can be seen by comparing the calculated π-bond orders of **4a**, **4b**, and 2-benzoylthiophene (Table IV).

There is additional evidence for a strong thiophene–carbonyl mesomeric interaction in the low frequency (1637 cm^{-1})[5] of the ir carbonyl band of **4b**. This band is identical with that reported for 2-benzoylthiophene[22] (1636 cm^{-1}), and a comparison with the usual carbonyl stretching frequency of diaryl ketones[23] (1670–1660 cm^{-1}) serves to illustrate the powerful mesomeric influence of the thiophene system. The carbonyl frequencies of substituents in the 3 position of thiophene are 16–18 cm^{-1} larger than the bands for the corresponding 2-substituted compounds,[22,24] which suggests a decrease in the thiophene–carbonyl interaction for 3 *vs.*

(19) See ref 4b, p 115.

(20) H. C. Longuet-Higgins, *Trans. Faraday Soc.,* **45,** 173 (1949).

(21) $\beta_{2-13} = 0.932\,\beta_0$, $\beta_{13-14} = 0.756\,\beta_0$.

(22) S. Gronowitz, *Ark. Kemi,* **13,** 295 (1958).

(23) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, p 137.

(24) S. Gronowitz and A. Rosenberg, *Ark. Kemi,* **8,** 23 (1955).

Table II. Bond Lengths and Angles Involving Hydrogen[a]

Atoms	Length, Å
C(3)–H(3)	1.06 (7)
C(4)–H(4)	0.98 (5)
C(6)–H(6)	0.96 (6)
C(8)–H(8a)	0.85 (6)
C(8)–H(8b)	0.89 (5)
C(9)–H(9a)	1.01 (7)
C(9)–H(9b)	0.91 (6)
C(9)–H(9c)	0.89 (9)
C(10)–H(10)	0.95 (5)
C(11)–H(11a)	0.93 (7)
C(11)–H(11b)	0.95 (8)
C(11)–H(11c)	1.02 (8)
C(12)–H(12a)	1.14 (7)
C(12)–H(12b)	0.96 (8)
C(12)–H(12c)	0.84 (8)
C(15)–H(15)	0.96 (6)
C(16)–H(16)	0.88 (7)
C(18)–H(18)	1.03 (6)
C(19)–H(19)	0.90 (6)

Atoms	Angle, deg
C(2a)–C(3)–H(3)	113 (3)
C(4)–C(3)–H(3)	119 (3)
C(3)–C(4)–H(4)	115 (4)
C(5)–C(4)–H(4)	111 (4)
C(5)–C(6)–H(6)	119 (3)
C(6a)–C(6)–H(6)	111 (3)
C(7)–C(8)–H(8a)	114 (4)
C(7)–C(8)–H(8b)	109 (3)
C(8a)–C(8)–H(8a)	111 (4)
C(8a)–C(8)–H(8b)	114 (3)
H(8a)–C(8)–H(8b)	108 (5)
C(7)–C(9)–H(9a)	114 (4)
C(7)–C(9)–H(9b)	104 (5)
C(7)–C(9)–H(9c)	101 (6)
H(9a)–C(9)–H(9b)	116 (6)
H(9a)–C(9)–H(9c)	111 (7)
H(9b)–C(9)–H(9c)	109 (7)
C(5)–C(10)–H(10)	104 (3)
C(11)–C(10)–H(10)	109 (3)
C(12)–C(10)–H(10)	107 (3)
C(10)–C(11)–H(11a)	112 (4)
C(10)–C(11)–H(11b)	109 (5)
C(10)–C(11)–H(11c)	115 (4)
H(11a)–C(11)–H(11b)	100 (7)
H(11a)–C(11)–H(11c)	106 (6)
H(11b)–C(11)–H(11c)	115 (6)
C(10)–C(12)–H(12a)	105 (4)
C(10)–C(12)–H(12b)	111 (5)
C(10)–C(12)–H(12c)	109 (6)
H(12a)–C(12)–H(12b)	101 (6)
H(12a)–C(12)–H(12c)	124 (7)
H(12b)–C(12)–H(12c)	106 (7)
C(14)–C(15)–H(15)	114 (4)
C(16)–C(15)–H(15)	123 (4)
C(15)–C(16)–H(16)	120 (4)
C(17)–C(16)–H(16)	120 (4)
C(17)–C(18)–H(18)	121 (3)
C(19)–C(18)–H(18)	120 (3)
C(14)–C(19)–H(19)	115 (3)
C(18)–C(19)–H(19)	123 (3)

[a] Estimated standard deviations are in parentheses.

Table III. ω-HMO Delocalization Energies

Compd	Delocalization energy, β
3a	3.57
4a	3.34
3b	4.88
4b	5.06
C_6H_5CO	1.31

Table IV. ω-HMO π Bond Orders for Thiophene and Three Derivatives[a]

Bond	Thiophene	2-Benzoyl-thiophene	**4a**	**4b**
S–C(2)	0.58	0.53	0.59	0.53
S–C(8a)	0.58	0.57	0.58	0.56
C(2)–C(2a)	0.73	0.66	0.66	0.59
C(8a)–C(8b)	0.73	0.72	0.69	0.69
C(2a)–C(8b)	0.61	0.63	0.51	0.51
C(2a)–C(3)			0.45	0.48
C(3)–C(4)			0.78	0.76
C(4)–C(5)			0.51	0.52
C(5)–C(6)			0.78	0.77
C(6)–C(6a)			0.45	0.46
C(6a)–C(7)			0.80	0.80
C(6a)–C(8b)			0.37	0.37
C(2)–C(13)		0.41		0.43
C(13)–C(14)		0.31		0.31
O–C(13)		0.83		0.81
C(14)–C(15)		0.63		0.63
C(14)–C(19)				
C(15)–C(16)		0.67		0.67
C(18)–C(19)				
C(16)–C(17)		0.66		0.66
C(17)–C(18)				

[a] The atom numbering system is the one used in Figure 1.

7 was obtained from the acid-catalyzed cyclodehydration of 6,8-dimethyl-4-methylsulfinylmethylazulene (6).[25] The visible absorption spectrum of compound 8 (principal maximum at 647 nm) was that expected for a
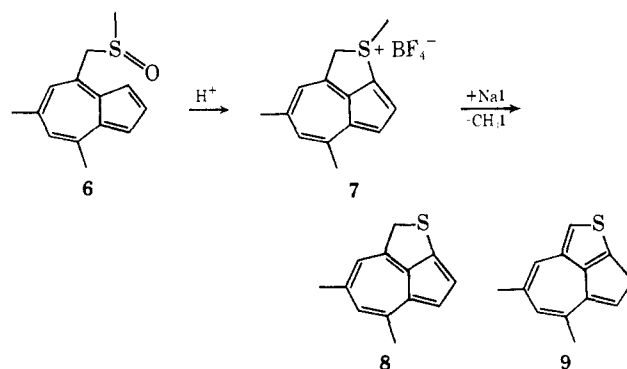
1-alkylthio-substituted azulene.[26] Compound 9 would be expected to have a visible spectrum similar to that of 4b with a maximum near 500 nm. The assignment of structure 7 is further supported by the difference in the chemical shifts of the methylene protons observed in this compound, τ 5.16,[27] and that found for compound 4b, τ 6.8. Evidence for the greater stability of 8 relative to 9 was obtained from an experiment which showed that there was no change in the visible or near-ultra-

2 substituents. The relative magnitudes of the π-bond orders computed for 2- and 3-formyl- and for 2- and 3-benzoythiophenes parallel this trend.

Further confirmation that the benzoyl group is responsible for the inversion of the relative stabilities of 3 and 4 has resulted from the synthesis of a new derivative of the azuleno[1,8-bc]thiophene system, viz. 4,6-dimethyl-2H-azuleno[1, 8-bc]thiophene (8), prepared by the demethylation of the sulfonium salt 7.[25] Compound

(25) L. L. Replogle, R. Frost, and J. M. Porter, unpublished.

(26) L. L. Replogle, R. M. Arluck, and J. R. Maynard, *J. Org. Chem.*, **30**, 2715 (1965).

(27) The nmr spectrum of a similar (noncyclic) sulfide 4,6-dimethyl-8-phenylthiomethylazulene shows the methylene resonance at τ 5.53.[25]

violet spectrum of a methanolic solution of the material with the addition of sodium hydroxide.

Dimer. The reaction of the thiocyano ketone **5a** with potassium hydroxide in the presence of air gave a red, crystalline compound (63% yield) which was not identical with **4b**. This high-melting solid (215-215.5°) is insoluble in water and most organic solvents, but is very slightly soluble in chloroform and dichloromethane. Its uv-visible spectrum is very similar to that of **4b** with a maximum in the visible at 495 nm. The nmr spectrum is also very similar to that of **4b** except that the CH_2 peak of **4b** at τ 6.78 has been replaced by a peak of unit area at τ 6.23. These data are strong evidence that the substance is the dimer **10**. The elemental analysis and X-ray molecular weight are also in accord with the proposed structure.

PhCO   COPh

10
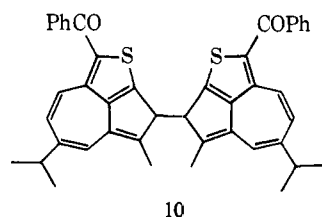
The dimer can also be obtained by treatment of the monomer **4b** with base in the presence of air. Therefore, it seems probable that the formation of **10** from **5a** involves **4b** as an intermediate. Presumably, the base forms the anion of **4b** which in turn is oxidized by oxygen in the air to a free radical which can then couple to give the dimer **10**. In support of this proposal was the observation that treatment of **4b** with base under the same conditions as before except for the exclusion of air gave mostly unreacted starting material and only a very low yield of dimer.

Crystal Structure of 2-(p-Bromobenzoyl)-5-isopropyl-7-methyl-8H-azuleno[1,8-bc]thiophene (4c). The results from the calculations of some least-squares planes are given in Table V. The carbonyl group and the benzene, thiophene, and heptafulvenothiophene rings are each coplanar within experimental error. Relatively large deviations from the plane of the three fused rings are found for the isopropyl methine (C-10) and the carbonyl carbons (C-13). The dihedral angles about the benzene-carbonyl and heptafulvenothiophene-carbonyl bonds were found to be, respectively, 41.1 and 17.0°.

The exocyclic angles at the carbon atoms linked to the methyl, isopropyl, and benzoyl groups are all similar in that one of the angles in each pair is 5-7° greater than the other. Each of these central atoms forms one end of a C-C double bond and in all three cases the larger of the two exocyclic angles is adjacent to the double bond, a type of arrangement which is characteristic of the C=C linkage.[28,29] There does not appear to be an obvious rationale for the exocyclic bond angle asymmetry at C-14 of the benzene ring.

The isopropyl group is found in a symmetrical conformation relative to the 7-ring plane (Figure 2) with a methyl group on each side of the ring. The dihedral angles about the C(5)-C(10) bond for C(12)···C(4) and

(28) Just one example is 2,3-dimethylbutadiene which has C=C—C and C—C—C angles of 122.0 and 117.9°, respectively.[29]

(29) C. F. Aten, L. Hedberg, and K. Hedberg, *J. Amer. Chem. Soc.*, **90**, 2463 (1968).
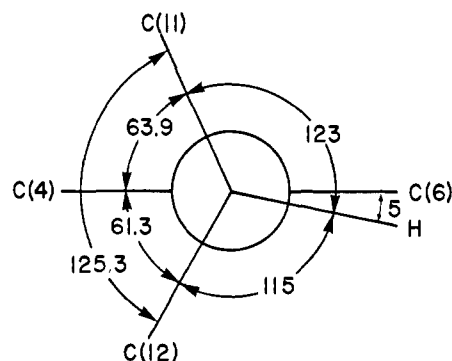
Figure 2. A projection showing the conformation of the isopropyl group relative to the seven-membered ring. The dihedral angles (degrees) are reported.

C(11)···C(4) are, respectively, 64 and 61°, an arrangement which maximizes the nonbonded distances between the methyls and C(4). A 90° rotation of the isopropyl group about the C(5)-C(10) bond would lead to another staggered conformation with two CH_3···C(4) and CH_3···C(6) dihedral angles of about 30°. Clearly, this conformation is less stable than the first one since it results in a decrease in the CH_3···C nonbonded distances.

Table V. Displacements (Å) from the Least-Squares Planes[a]

Atom	Plane 1	Plane 2	Plane 3	Plane 4
S	−0.040	0.002		−0.526[b]
C(2)	−0.031	−0.002	−0.809[b]	−0.006
C(2a)	0.006	0.002		0.200[b]
C(3)	0.058	0.035[b]		
C(4)	0.043	−0.013[b]		
C(5)	−0.078	−0.162[b]		
C(6)	−0.052	−0.134[b]		
C(6a)	0.031	−0.023[b]		
C(7)	0.045	−0.007[b]		
C(8)	0.001	−0.017[b]		
C(8a)	−0.002	−0.001		
C(8b)	0.020	0.000		
C(9)	0.094[b]			
C(10)	−0.269[b]			
C(11)	0.877[b]			
C(12)	−1.606[b]			
C(13)	−0.215[b]	−0.161[b]	0.032[b]	0.018
O	−0.600[b]		0.726[b]	−0.007
C(14)	−0.015[b]		−0.007	−0.006
C(15)			0.013	−0.792[b]
C(16)			−0.006	
C(17)			−0.008	
C(18)			0.013	
C(19)			−0.006	0.762[b]
Br			0.004[b]	

[a] Equation of plane 1, $-2.8528x + 8.1652y + 12.1760z = 7.8468$; equation of plane 2, $-2.7878x + 8.3361y + 11.8170z = 7.6973$; equation of plane 3, $5.3875x + 5.4150y + 9.4290z = 8.0931$; equation of plane 4, $-0.7058x + 7.2986y + 14.1970z = 9.0149$. [b] These atoms were not included in the plane calculations.

The mean of the six carbon–carbon distances in the *p*-bromobenzoyl group is 1.384 Å. Although the difference between this length and the 1.397 Å in benzene is not statistically significant, a parallel trend is shown by the *p*-bromophenyl group in other molecules For example, the appropriate C-C bond length averages in the *p*-bromophenylurethane derivative of 2-hydroxy-2-phenylbicyclo[1.1.1]pentane and in α-3-*p*-bromoben-

zoyloxy(cyclopentadiene dimer) are, respectively, 1.378[30] and 1.38 Å.[31,32]

The C(3)-C(4)-C(5)–C(6)–C(6a)–C(7) moiety shows the single-double bond alternation which is characteristic of acyclic hexatrienes[33] and of other conjugated alkenes.[34] These kinds of molecules frequently show double bond distances as long as the C(6a)-C(7) length of 1.363 Å and sp^2–sp^2 single bond lengths as short as the 1.427 Å observed for C(6)–C(6a).

The mesomeric interaction of the p-bromobenzoyl group with the thiophene ring is reflected by the bond distances in the sulfur heterocycle. Although the thiophene bond length pattern in **4b** cannot be easily rationalized on the grounds of a large contribution of structure **11b** to the ground-state resonance hybrid, there is good qualitative agreement with HMO π bond orders. The bond orders computed for both **4b** and 2-benzoylthiophene predict that S–C(8a), C(2a)–C(8b), and C(2)–

11a ⇌ 11b
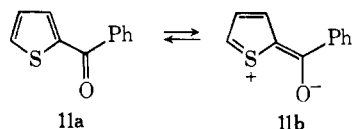
C(13) will be shorter, respectively, than S–C(2), C(2)–C(2a), and C(13)–C(14), and this trend is found in the observed bond lengths. There is, however, no simple quantitative relationship between the bond orders calculated for **4b** and for thiophene, and the bond distances in these molecules.[35] It is interesting to note that the bond orders obtained for the unsubstituted heptafulvenothiophene **4a** show very little of the asymmetry found in the thiophene ring of **4b** but that the asymmetry returns on substitution of a formyl group at C(2). The effects of conjugation of the benzene and heptafulvenothiophene moieties with the carbonyl can be seen in the π bond orders and these interactions may be reflected by the C–O distance of 1.233 Å. Although longer than the 1.215-Å average reported[37] for unconjugated aldehydes and ketones, this length is in line with C–O distances in aryl ketones.[38] In all of the above dis-

cussion, cognizance was taken only of the π bond orders and no account was made of effects arising from the σ bond network or from the molecular geometry.[39]

If it is assumed that coplanarity of the carbonyl and thiophene is the most stable arrangement for these groups, then there are two possible conformations about the benzoyl–heptafulvenothiophene bond. One possible arrangement places the benzene opposite to the thiophene while the other has the benzene and seven-membered ring in close juxtaposition. Molecular models clearly show that the latter conformation is the least stable of the two since it involves substantial non-bonded contacts between the benzene and seven-membered rings. The observed conformation is essentially the first one with a 56° angle between the benzene and thiophene rings, an angle which has probably been forced to relieve the S···C(19) and S···H(19) contacts.[40] The conformation places the carbonyl oxygen opposite the seven-membered ring and produces an H(3)···O distance, 2.36 Å, which is smaller than the 2.6-Å sum of the hydrogen and oxygen van der Waals radii. The existence of C–H···O hydrogen bonds seems controversial. Hamilton and Ibers[41] have classified this kind of interaction as a weak hydrogen bond and they have cited an average O···H distance of 2.3 Å, whereas Donohue[42] considers that O···H contacts as short as 2.2 Å cannot be interpreted in terms of hydrogen bond formation. In the present case, the hydrogen and oxygen atoms are on opposite sides of the three-ring plane and deviate from the plane by 0.3 and 0.6 Å, respectively. From these data, at least, it would appear that the interaction is repulsive in nature and hence should not be classed as a hydrogen bond.

(30) A. Padwa, E. Shefter, and E. Alexander, *J. Amer. Chem. Soc.*, 90, 3717 (1968).

(31) R. Destro, C. M. Gramaccioli, and M. Simonetta, *Chem. Commun.*, 568 (1968).

(32) In all of these cases, the substituent para to the bromine has trigonal hybridization.

(33) Table 3 in M. Traetteberg, *Acta Chem. Scand.*, 22, 628 (1968).

(34) 15,15'-Dehydrocanthaxanthin, J. C. J. Bart and C. H. MacGillavry, *Acta Crystallogr., Sect. B*, 24, 1569 (1968); canthaxanthin, J. C. J. Bart and C. H. MacGillavry, *ibid., Sect. B*, 24, 1587 (1968).

(35) The results of several electron diffraction and microwave studies of thiophene[36] are only in fair accord, but judicious averaging of these data has indicated C—S, C=C, and C—C distances of 1.715, 1.369, and 1.428 Å, respectively.

(36) B. Bak, D. Christensen, J. Rastrup-Anderson, and E. Tannenbaum, *J. Chem. Phys.*, 25, 892 (1956); B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Anderson, *J. Mol. Spectrosc.*, 7, 58 (1961); R. A. Bonham and F. A. Momany, *J. Phys. Chem.*, 67, 2474 (1963); W. Harshbarger and S. H. Bauer, Abstracts, American Crystallographic Association Meeting, Summer 1968, p 36.

(37) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," Supplement 1956–1959, The Chemical Society, London, England, 1965, p S21s.

(38) The C–O distance in benzophenone is 1.23 Å and the angle between the benzene rings is 56°: E. B. Fleischer, N. Sung, and S. Hawkinson, *J. Phys. Chem.*, 72, 4311 (1968).

(39) Consideration of the dihedral angles about C(2)–C(13) and C(13)–C(14) was made on defining the resonance integrals for these bonds.

(40) The S···H(19) and S···C(19) distances are 2.88 and 3.18 Å, respectively.

(41) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, pp 16 and 182.

(42) J. Donohue in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, p 443.