# Absorption Spectra and Structure of Substituted Benzo[*b*]thiin-4-one 1,1-Dioxides as New Chromophores

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The absorption spectra of 2- and 3-substituted benzo[*b*]thiin-4-one 1,1-dioxides have been studied to characterise their chromophores. From PPP MO calculations with the parameters empirically adjusted from the *X*-ray analysis, the first absorption bands of these derivatives are approximated by HOMO–LUMO transition, which involves the charge transfer from the donor group to the carbonyl group. It is found that the sulphonyl group plays a less significant role in the first absorption band. This finding is supported by *ab initio* calculations using STO-3G and STO-3G* basis sets and from results of resonance Raman spectroscopy and *X*-ray analysis.

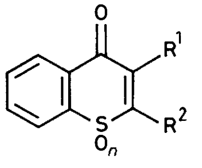
4*H*-Thiin-4-one 1,1-dioxides and their 4-(dicyanomethylene) derivatives are of interest in research on organic photoconductors as a potential new class of organic electron acceptors.[1] A new near-infrared absorption azo dye[2] was obtained by a suitable combination of donor substitution and a powerful acceptor containing a sulphonyl group during research on optical data-storage media. A commercial dye containing the sulphonyl group in a heterocyclic ring has been reported.[3] Though these compounds have a sulphonyl group in a heterocyclic ring as a strong electron-withdrawing group, the role of the sulphonyl group in chromophores has been little explored.[4]

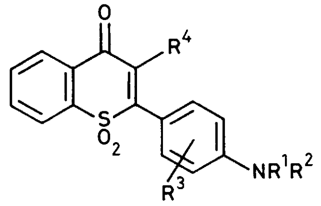
We have prepared various 2-alkylamino, 3-arylamino, and 2-arylbenzo[*b*]thiin-4-one (thiochromone) 1,1-dioxides,[5] which can be viewed as examples of a simple donor–acceptor system and sulphone analogues of 1,4-naphthoquinone dyes. These derivatives display an irreversible reduction wave in their cyclic voltammograms, whereas 1,4-naphthoquinone shows two reversible one-electron reduction waves. This result suggests that thiochromone 1,1-dioxides are chromophores remarkably different from 1,4-naphthoquinones.

In this paper, we have investigated the absorption spectra of the substituted thiochromone 1,1-dioxides to characterize their chromophores and have interpreted them with the aid of molecular-orbital calculations, resonance Raman spectroscopy, and *X*-ray analysis.

## Results and Discussion

*Absorption Spectra and Molecular-orbital Calculations.*—The absorption spectra of compounds (**1**)–(**26**) in chloroform are summarized in Table 1. The longest wavelength absorption band of thiochromone 1,1-dioxides is assigned to the $\pi$–$\pi^*$ transition by its intensity ($\varepsilon > 10^3$). The 2- or 3-amino substitution of (**1**) cause a bathochromic shift of the longest wavelength band by 66 nm to 146 nm and an increase in intensity. The 2-aryl substitution of (**1**) gave a significant bathochromic shift of 170 nm to 224 nm. A similar bathochromic shift by substitution has been observed for 1,4-naphthoquinones.[6,7] This remarkable bathochromic shift may be caused by extended conjugation through the phenyl bridge between an amino group and a thiopyran ring. Aryl compounds have lower intensities, compared with the alkylamino and anilino compounds (**2**)–(**8**). This feature may be attributed to greater steric crowding of an aryl group. Additional steric crowding by the 2-methyl group of the 2-aryl residue gave a reduction in intensity shown by comparison with the ε values with those of (**21**) and (**25**).





(**1**) $R^1 = Br, R^2 = Br, n = 2$
(**2**) $R^1 = Br, R^2 = NHMe, n = 2$
(**3**) $R^1 = Br, R^2 = NMe_2, n = 2$
(**4**) $R^1 = Br, R^2 = NHPh, n = 2$
(**5**) $R^1 = Br, R^2 = 4\text{-}MeOC_6H_4NH, n = 2$
(**6**) $R^1 = Br, R^2 = 4\text{-}MeC_6H_4NH, n = 2$
(**7**) $R^1 = Br, R^2 = 4\text{-}AcC_6H_4NH, n = 2$
(**8**) $R^1 = Br, R^2 = 4\text{-}O_2NC_6H_4NH, n = 2$
(**9**) $R^1 = Br, R^2 = N(Me)Ph, n = 2$
(**10**) $R^1 = Br, R^2 = 3,5\text{-}Me_2C_6H_3NMe, n = 2$
(**11**) $R^1 = NHPh, R^2 = H, n = 1$
(**12**) $R^1 = NHPh, R^2 = H, n = 2$
(**13**) $R^1 = 4\text{-}MeC_6H_4NH, R^2 = H, n = 1$
(**14**) $R^1 = 4\text{-}MeC_6H_4NH, R^2 = H, n = 2$
(**15**) $R^1 = 4\text{-}O_2NC_6H_4NH, R^2 = H, n = 1$
(**16**) $R^1 = 4\text{-}O_2NC_6H_4NH, R^2 = H, n = 2$
(**17**) $R^1 = NH_2, R^2 = H, n = 2$
(**18**) $R^1 = Me, R^2 = H, R^3 = H, R^4 = Br$
(**19**) $R^1 = Et, R^2 = H, R^3 = H, R^4 = Br$
(**20**) $R^1 = Ph, R^2 = H, R^3 = H, R^4 = Br$
(**21**) $R^1 = Me, R^2 = Me, R^3 = H, R^4 = Br$
(**22**) $R^1 = Et, R^2 = Et, R^3 = H, R^4 = Br$
(**23**) $R^1 = Et, R^2 = Et, R^3 = H, R^4 = H$
(**24**) $R^1 = Me, R^2 = H, R^3 = 3\text{-}Me, R^4 = Br$
(**25**) $R^1 = Me, R^2 = Me, R^3 = 2\text{-}Me, R^4 = Br$
(**26**) $R^1 = Et, R^2 = Et, R^3 = 2\text{-}Me, R^4 = Br$

It is noteworthy that the values of ε of the 3-substituted derivatives (**12**), (**14**), and (**16**) are *ca.* 2.5 times larger than those of the corresponding 2-substituted derivatives (**4**), (**6**), and (**8**). The anilino group of the latter suffers steric strain from a bromine atom in the 3-position. The advantage of absorption intensity on 3-arylamino compounds may be dependent on the planar structure, rather than the position of substituents, because a debromo compound (**23**), which has no steric crowding of the substituents between the 2- and 3-positions, has exceptional intensity in 2-substituted derivatives. Comparison of the absorption maxima of the pairs of (**11,12**), (**13,14**), and (**15,16**) shows that replacement of the sulphoxide function of thiochromone 1-oxide with a sulphonyl group leads to a slight hypsochromic shift and an increase in intensity.

Comparison of the longest wavelength absorption bands of thiochromone 1,1-dioxides and related 1,4-naphthoquinones shows that replacement of one carbonyl group of 1,4-naphthoquinone by the sulphonyl group leads to a remarkably large hypsochromic shift and an increase in absorption intensity, as shown in Table 2. The smallest hypsochromic shift was observed for the aryl-substituted compound (**21**).

The PPP MO calculation using optimum parameters for typical substituted thiochromone 1,1-dioxides showed excellent agreement between calculated and experimental absorption bands. From the CI calculation, the first transitions of these derivatives were approximated by HOMO–LUMO transition. Figure 1 shows the PPP MO calculated HOMO and LUMO energy levels together with results of *ab initio* calculations with a STO-3G basis set. A good correlation exists between the PPP MO and *ab initio* calculations. Substitution by aniline in the 2- or 3-position of (**1**) causes predominantly a raising of the HOMO rather than the LUMO, and results in a bathochromic shift. A remarkable bathochromic shift by 2-arylation is caused to a large extent by an increase in the HOMO energy level. A larger bathochromic shift of 3-substituted derivative (**12**), compared with 2-substituted derivative (**4**), was reproduced well by PPP calculation.

The LCAO (linear combination of atomic orbitals) coefficients of the HOMO and LUMO of (**21**) and the π-electron density changes for the first excitation are shown in Figures 2 and 3, respectively. The HOMO and LUMO calculated by *ab initio* methods consist of mostly $p_\pi$ orbitals shown in Figure 2. The coefficients of the HOMO and LUMO calculated by the

**Table 1.** Observed and calculated absorption spectra of substituted thiochromone 1,1-dioxides and 1-oxides.

| | Observed | | Calculated[a] | |
|---|---|---|---|---|
| Compound | $\lambda_{max.}(CHCl_3)$/nm | $\varepsilon$/dm$^{-3}$ mol$^{-3}$ cm$^{-1}$ | $\lambda_{max.}$/nm | $f$ |
| (**1**) | 299 | 2 640 | 298 | 0.23 |
| (**2**) | 365 | 9 100 | | |
| (**3**) | 402 | 7 720 | | |
| (**4**) | 373 | 9 350 | 374 | 0.16 |
| (**5**) | 372 | 8 990 | | |
| (**6**) | 373 | 9 370 | | |
| (**7**) | 382 | 10 900 | | |
| (**8**) | 382 | 15 000 | | |
| (**9**) | 438 | 5 500 | | |
| (**10**) | 445 | 4 000 | | |
| (**11**) | 387 | 22 600 | | |
| (**12**) | 381 | 25 200 | 381 | 0.02 |
| (**13**) | 391 | 23 100 | | |
| (**14**) | 388 | 23 300 | | |
| (**15**) | 398 | 37 800 | | |
| (**16**) | 389 | 41 600 | | |
| (**17**) | 375 | 1 650 | | |
| (**18**) | 471 | 6 220 | | |
| (**19**) | 476 | 6 790 | | |
| (**20**) | 469 | 6 270 | | |
| (**21**) | 501 | 7 520 | 499[b] | 0.14 |
| (**22**) | 517 | 9 520 | | |
| (**23**) | 490 | 24 200 | | |
| (**24**) | 480 | 5 850 | | |
| (**25**) | 504 | 2 060 | | |
| (**26**) | 523 | 2 230 | | |

[a] The PPP MO calculations were performed on representative derivatives (**1**), (**4**), (**12**), and (**21**). [b] Values of $E_i$ = 23.00 and $\gamma_{rr}$ = 17.44 eV for nitrogen atom were used.

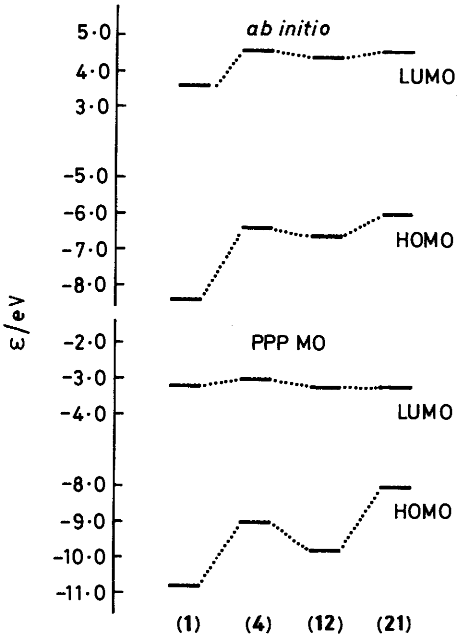
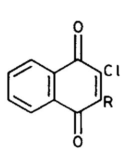
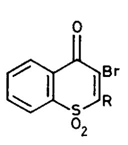


**Figure 1.** PPP–MO and *ab initio* calculated HOMO and LUMO energy levels.

**Table 2.** Visible absorption spectra of benzo[*b*]thiin-4-one 1,1-dioxides and related 1,4-naphthoquinones.





| | 1,4-naphthoquinones | | thiochromone 1,1-dioxides [(**2**), (**3**), (**4**), and (**21**)] | | | |
|---|---|---|---|---|---|---|
| R | $\lambda_1$[a]/nm | $\varepsilon_1 \times 10^{-3}$[a] | $\lambda_2$[a]/nm | $\varepsilon_2 \times 10^{-3}$[a] | $\Delta(\lambda_1 - \lambda_2)$[b] | $\varepsilon_2/\varepsilon_1$ |
| NHMe | 472 | 3.08 | 365 | 9.10 | 107 | 3.0 |
| $NMe_2$ | 499 | 3.64 | 402 | 7.72 | 97 | 2.1 |
| NHPh | 480 | 4.61 | 373 | 9.35 | 107 | 3.0 |
| $4-Me_2NC_6H_4$ | 527[c,d] | 4.40[c,d] | 501 | 7.52 | 26 | 1.7 |

[a] In chloroform. [b] The difference between chlorine and bromine in the 2- or 3-position of thiochromone 1,1-dioxides is ignored as its effect on the longest-wavelength band is very small (*ca.* 4–6 nm). [c] In toluene. [d] Ref. 7.

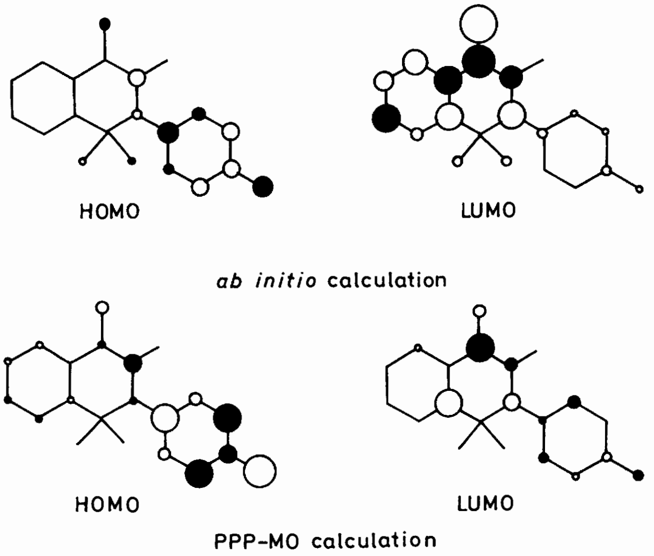


**Figure 2.** Presentation of the expansion coefficients of HOMOs and of LUMOs (**21**). The open (shaded) circle signifies that the positive (negative) lobe of the $p_\pi$ orbital is above the molecular plane. Their areas indicates the magnitude of the sequences of the expansion coefficients.

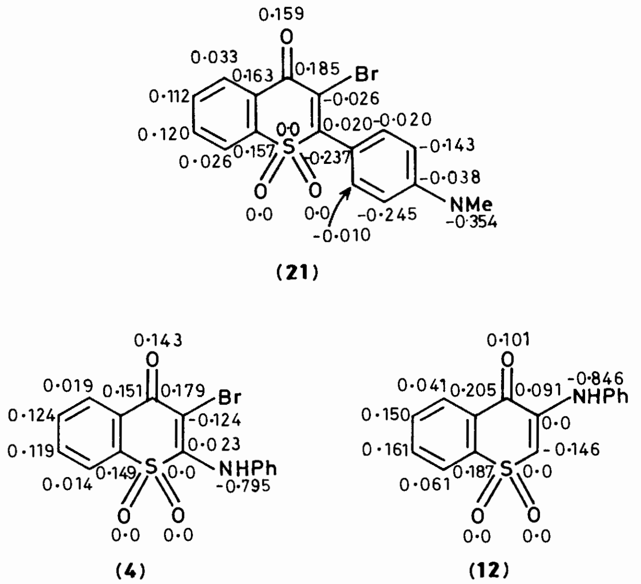


**Figure 3.** π-Electron-density changes for the first-electron transition of (**4**), (**12**), and (**21**).

PPP method are in reasonable agreement with those calculated by the *ab initio* calculation with a STO-3G basis set, except for those for the benzene moiety fused to a thiopyran ring in the LUMO. As for the high expansion coefficients of the amino and 2-phenyl groups in the HOMO shown by both calculations (Figure 2), the amino and phenyl group act mainly as electron donors in the lowest energy excitation. The high expansion coefficients of the carbonyl group and the thiine ring (except for the sulphonyl group) in the LUMO in both calculations were shown. This implies that the carbonyl group acts mainly as an electron acceptor in the lowest energy excitation. However, the expansion coefficients of the sulphonyl group are *ca.* zero. This shows that the sulphonyl group does not act as an acceptor in the lowest energy excitation. Although *ab initio* calculations with a STO-3G* level, including 3d orbitals of sulphur, were carried out, the high expansion coefficients of the sulphonyl group were not calculated. The results were similar to those using a STO-3G basis set.

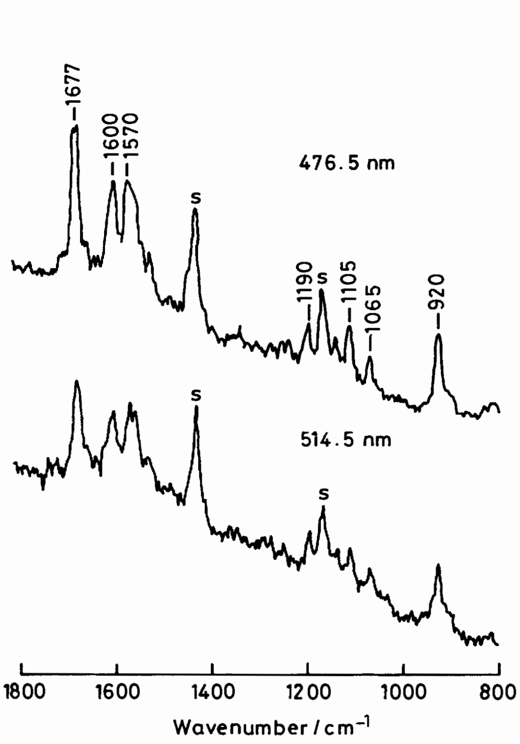


**Figure 4.** Resonance Raman spectra of (**18**) using excitation at 476.5 and 514.5 nm. The bands marked 'S' are due to dichloromethane.

In the PPP calculations including the CI treatment, π-electron density changes in the one-electron transition responsible for the first absorption band of (**21**) which shows typical charge-transfer character are similar to those of the corresponding 1,4-naphthoquinones.[6,7] Thus, a visible absorption band of 2-aryl derivatives could be attributed to an electronic transition involving a migration of electron density from the alkylamino group to the carbonyl group and the phenyl residue fused thiine ring, which is classified as a simple donor–acceptor chromophore.[8] Also π-electron density changes for anilino derivatives (**4**) and (**12**) show the charge migration from the donor group to the carbonyl group.

*Resonance Raman Spectra of Thiochromone* 1,1-*Dioxides* (**18**) *and* (**21**).—In order to study the intensity behaviour of vibrations resonated by a transition where a carbonyl or a sulphonyl group is present, we measured the Raman excitation profile from 800–1 800 $cm^{-1}$ (Figure 4).

The band at 1 677 $cm^{-1}$ in (**18**) is assigned to the vibrations of carbonyl stretching and the bands at 1 600 and 1 570 $cm^{-1}$ are assigned to the vibrations of benzene ring stretching. These became the most intense bands when irradiated at 476.5 nm, this wavelength is close to the absorption maximum of (**18**) ($\lambda_{max.}$ 471 nm). For example, the intensity at 1 677 $cm^{-1}$ for (**18**) excited with the 476.5 nm laser line is about 1.6 times larger than with the 514.5 nm laser line. The enhancement of Raman intensities at 1 600 and 1 570 $cm^{-1}$ was also observed. Similar resonance Raman spectra for (**21**) at 1 675, 1 600, and 1 565 $cm^{-1}$ were observed. However, there are no frequency peaks in the 1 200–1 400 $cm^{-1}$ range, which may be assigned to symmetric or unsymmetric stretching vibrations of a sulphonyl group. These results show that in the thiochromone 1,1-dioxide chromophore the carbonyl function contributes to the colour development to a greater extent than the sulphone function. This conclusion is consistent with that of the above MO calculations.

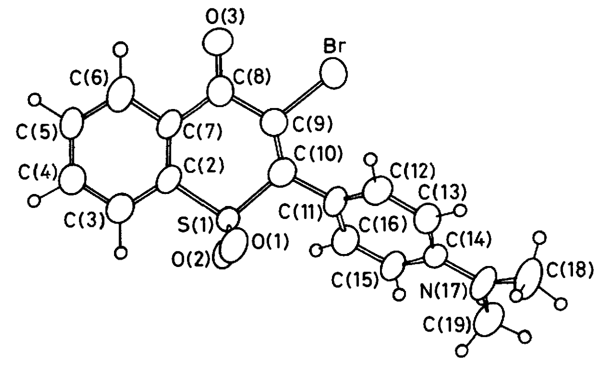


**Figure 5.** ORTEP drawing of (**21**) showing the atom labelling scheme.

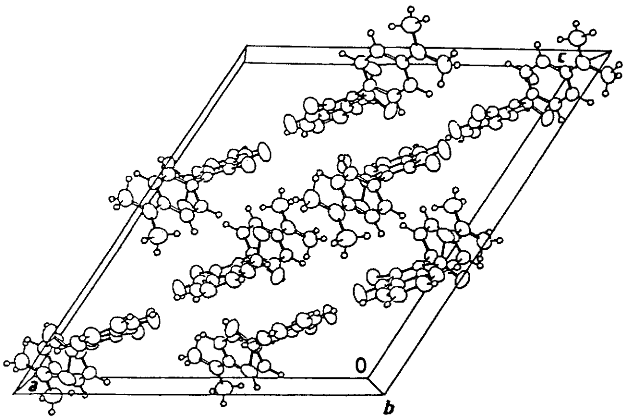


**Figure 6.** Projection of the molecular packing of (**21**).

**Table 3.** Bond distances/Å [a].

| | | | |
|---|---|---|---|
| S(1)–O(1) | 1.427(7) | C(9)–C(10) | 1.278(16) |
| S(1)–O(2) | 1.419(6) | C(9)–Br | 1.908(9) |
| S(1)–C(2) | 1.766(10) | C(10)–C(11) | 1.491(14) |
| S(1)–C(10) | 1.797(9) | C(11)–C(12) | 1.417(10) |
| C(2)–C(3) | 1.407(13) | C(11)–C(16) | 1.401(13) |
| C(2)–C(7) | 1.353(17) | C(12)–C(13) | 1.405(15) |
| C(3)–C(4) | 1.385(17) | C(13)–C(14) | 1.414(13) |
| C(4)–C(5) | 1.377(22) | C(14)–C(15) | 1.413(11) |
| C(5)–C(6) | 1.417(14) | C(14)–N(17) | 1.381(14) |
| C(6)–C(7) | 1.422(15) | N(17)–C(18) | 1.478(12) |
| C(7)–C(8) | 1.514(13) | N(17)–C(19) | 1.464(15) |
| C(8)–C(9) | 1.527(14) | C(15)–C(16) | 1.395(15) |
| C(8)–O(3) | 1.206(17) | | |

[a] Numbers in parentheses are the standard deviations.

*X-Ray Single-crystal Analysis of Thiochromone* 1,1-*Dioxide* (**21**).—*X*-Ray analysis has been applied to the measurement of the bond distance between sulphur and carbon (sp$^2$) as a measure of the conjugation of the sulphonyl group with the p$_\pi$ system.[9] We have applied *X*-ray single-crystal analysis to a typical red thiochromone 1,1-dioxide chromophore (**21**).

Figure 5 shows the molecule with atomic labelling and bond distances shown in Table 3. Bond angles, positional parameters, and thermal parameters are given in supplementary tables.

The C–S bond lengths (1.77 and 1.80 Å) in (**21**) are longer than the *ca.* 1.70 Å found for the conjugated C(sp$^2$)–SO$_2$ bond and the *ca.* 1.75 Å found for the standard C–SO$_2$ bond.[9,10] This result suggests that there is very little overlap of the sulphur with the π-system in the ground state of thiochromone 1,1-dioxide. Despite the steric crowding between the 2- and 3-substituents, the C(9)–C(10) bond length is unusually shorter than a normal double bond (1.34 Å). The thiine ring is approximately planar with deviations between −0.002 and 0.02 Å from the least-squares plane which consists of C(2), C(7), C(8), C(9), C(10), and sulphur. An aryl group in the 2-position of (**21**) describes a dihedral angle of 63.0° and is obviously not coplanar with thiine ring. Figure 6 shows the molecular packing. The molecules pack plane-to-plane with overlapping between the carbonyl group and sulphonyl group. The closest contacts between the least-squares planes for the thiine ring are about 3.5 Å. There are no contacts less than the sum of van der Waals radii in the structure. This implies that there is little contribution from charge-separated canonical forms of the sulphonyl group to the structure represented formally by (**21**).

## Experimental

Electronic absorption spectra in the visible region were recorded on a Shimadzu UV-265FS spectrometer. Concentrations of approximately 1 × $10^{-4}$ or $10^{-5}$ mol dm$^{-3}$ thiochromone 1,1-dioxides in chloroform were used. Raman spectra were recorded on a Jasco NR-1000 spectrometer. To obtain the resonance Raman spectra of the thiochromone 1,1-dioxides, the solution was prepared in spectroscopic grade dichloromethane. Concentrations of the thiochromone (benzo[*b*]thiin-4-one) 1,1-dioxides were approximately 1 × $10^{-3}$ mol dm$^{-3}$. Each prepared solution, held in a spinning capillary tube, was irradiated with a NEC GLS 3200 argon ion laser emitting a power of 50 mW at 514.5 nm. The 1 425 cm$^{-1}$ peak of dichloromethane was used as an internal intensity reference at each excitation wavelength. It was assumed that the Raman scattering of dichloromethane did not undergo appreciable resonance enhancement.

*Materials.*—All substituted benzo[*b*]thiin-4-one 1,1-dioxides and 1-oxides used were prepared as previously described.[5]

*Molecular-orbital Calculations.*—The Pariser–Parr–Pople (PPP) method was used with the variable β approximation. Electronic excitation energies were similarly refined by a CI treatment as described previously.[11]

The ionization potential ($E_i$) and two-centre repulsion integral ($\gamma_{rr}$) for most of the atoms were as used elsewhere.[12,13] Parameters for the sulphonyl group are not known. The inductive effect of the sulfonyl group was adjusted by increasing the $E_i$ and electron affinity values of the adjacent carbon atoms C(2) and C(10). The inductive effect of the halogen atom was adjusted similarly by adjacent carbon atoms. Parameters for the sulphonyl group were empirically optimized until calculations for four typical benzo[*b*]thiin-4-one 1,1-dioxides reproduce all experimental values ($\lambda_{max.}$). However, experimental oscillator strengths of transitions cannot be reproduced satisfactorily, due to use of PPP–CI method with exclusion of 25 excited configurations. New parameters used are as follows; S: $E_i$ = 12.70 eV; $\gamma_{rr}$ = 9.94 eV; $\beta_{cs}$ = 0.0 eV, O(SO)$_2$: $E_i$ = 20.0 eV; $\gamma_{rr}$ = 17.73 eV; $\beta_{os}$ = −3.5 eV, C(2) and C(10): $E_i$ = 14.00 eV; $\gamma_{rr}$ = 11.30 eV, C(9): $E_i$ = 8.80 eV; $\gamma_{rr}$ = 8.77 eV, C(9) and C(10): $\beta_{cc}$ = −5.5 eV.

Other β values were adjusted at every interaction of the SCF calculations in accordance with the equations proposed by Nishimoto and Forstor.[14] These values for carbon–carbon bonds are −1.99 to *ca.* −2.41 eV. The fitting of absorption bands of four benzo[*b*]thiin-4-one 1,1-dioxides are relevant to whether a node at the sulphonyl group in molecular wavefunctions is defined, as $\beta_{cs}$ is 0.0 eV. Even if a small value is used as that of $\beta_{cs}$, the PPP–CI calculation fails to predict the

**Table 4.** Crystal data and collection condition for benzo[b]thiine-4-one.

| | |
|---|---|
| Formula | $C_{17}H_{14}BrNO_3S$ |
| Mol. wt. | 392.26665 |
| Crystal system | Monoclinic |
| Space group | *C*2/*c* |
| Cell constants, | |
| *a*/Å | 18.505(3) |
| *b*/Å | 10.036(2) |
| *c*/Å | 20.927(3) |
| β/deg | 123.307(8) |
| *V*/Å$^3$ | 3247.8(10) |
| *Z* | 8 |
| $d_{calcd}$/g cm$^{-3}$ | 1.603 |
| Crystal dimension/mm | 0.24 × 0.28 × 0.46 |
| Radiation (λ/Å) | Mo-*K*α(0.71069) |
| Scan techniques | ω–2θ |
| Scan speed/deg min$^{-1}$ | 2.9–29.3 |
| Total refections | 2484 |
| Unique reflections [$F_0 \geqslant 3\sigma(F)$] | 2000 |

**Table 5.** Atomic co-ordinates and thermal parameters.

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| S(1) | 0.423 3(1) | 0.391 6(2) | 0.621 4(1) |
| C(2) | 0.386 3(5) | 0.520 8(8) | 0.653 8(4) |
| C(3) | 0.414 5(6) | 0.649 4(9) | 0.650 6(5) |
| C(4) | 0.388 7(7) | 0.755 8(9) | 0.675 7(6) |
| C(5) | 0.339 4(6) | 0.735 8(9) | 0.705 8(5) |
| C(6) | 0.310 3(6) | 0.606 6(9) | 0.708 6(5) |
| C(7) | 0.335 8(5) | 0.498 9(8) | 0.681 0(4) |
| C(8) | 0.303 9(5) | 0.363 5(8) | 0.687 1(5) |
| C(9) | 0.329 0(5) | 0.245 0(8) | 0.657 4(4) |
| C(10) | 0.377 9(5) | 0.241 4(8) | 0.632 0(4) |
| C(11) | 0.402 1(5) | 0.124 2(8) | 0.603 7(5) |
| C(12) | 0.336 0(5) | 0.051 7(9) | 0.540 1(5) |
| C(13) | 0.358 1(6) | −0.058 2(8) | 0.512 6(5) |
| C(14) | 0.444 9(5) | −0.100 2(8) | 0.547 9(5) |
| C(15) | 0.510 1(5) | −0.024 4(9) | 0.610 0(5) |
| C(16) | 0.488 3(5) | 0.085 7(9) | 0.636 7(5) |
| N(17) | 0.466 0(5) | −0.211 5(7) | 0.522 6(4) |
| C(18) | 0.398 6(7) | −0.279 4(11) | 0.451 8(6) |
| C(19) | 0.556 5(7) | −0.252 3(10) | 0.560 1(6) |
| O(1) | 0.385 0(4) | 0.411 1(6) | 0.541 4(3) |
| O(2) | 0.514 8(3) | 0.384 2(6) | 0.669 5(4) |
| O(3) | 0.259 7(4) | 0.351 0(6) | 0.712 7(4) |
| Br | 0.280 7(1) | 0.084 5(1) | 0.667 4(1) |

absorption maxima for these compounds. The geometries for the various molecules studied were taken from *X*-ray structure data for **(4)**[15] and **(21)**.

*ab initio* STO-3G and STO-3G* calculations were carried out with the geometry taken from *X*-ray analysis within single-point calculations on a HITAC S810 computer with standard options in the GAUSSIAN 82[16] program system. To simplify this calculation we simulated the dimethyl amino group of **(21)** as an amino group and bromine atoms as chlorine atoms; the crystallographic parameters for **(4)** and **(21)** were used.

**Table 6.** Bond angles (deg)[a]

| | | | |
|---|---|---|---|
| O(1)–S(1)–O(2) | 118.0(6) | C(8)–C(9)–C(10) | 129.4(9) |
| O(1)–S(1)–C(2) | 107.6(4) | C(8)–C(9)–Br | 110.3(8) |
| O(1)–S(1)–C(10) | 107.2(4) | Br–C(9)–C(10) | 120.2(7) |
| O(2)–S(1)–C(10) | 109.0(4) | S(1)–C(10)–C(9) | 120.9(7) |
| C(2)–S(1)–O(2) | 109.2(4) | C(9)–C(10)–C(11) | 128.5(9) |
| C(2)–S(1)–C(10) | 105.2(5) | S(1)–C(10)–C(11) | 110.5(8) |
| S(1)–C(2)–C(3) | 115.0(10) | C(10)–C(11)–C(12) | 119.0(8) |
| C(3)–C(2)–C(7) | 121.9(10) | C(10)–C(11)–C(16) | 122.0(7) |
| S(1)–C(2)–C(7) | 123.1(7) | C(12)–C(11)–C(16) | 118.9(9) |
| C(2)–C(3)–C(4) | 118.4(13) | C(11)–C(12)–C(13) | 119.5(9) |
| C(3)–C(4)–C(5) | 120.9(10) | C(12)–C(13)–C(14) | 121.5(7) |
| C(4)–C(5)–C(6) | 120.9(11) | C(13)–C(14)–C(15) | 118.1(9) |
| C(5)–C(6)–C(7) | 117.4(12) | C(13)–C(14)–N(17) | 121.3(7) |
| C(6)–C(7)–C(2) | 120.5(9) | C(15)–C(14)–N(17) | 120.6(9) |
| C(6)–C(7)–C(68) | 114.6(10) | C(14)–N(17)–C(18) | 119.8(9) |
| C(8)–C(7)–C(2) | 124.9(9) | C(14)–N(17)–C(19) | 120.1(7) |
| C(7)–C(8)–C(9) | 116.4(10) | C(18)–N(17)–C(19) | 119.6(10) |
| C(7)–C(8)–O(3) | 121.4(9) | C(14)–C(15)–C(16) | 120.4(9) |
| C(9)–C(8)–O(3) | 122.1(9) | C(15)–C(16)–C(11) | 121.5(7) |

[a] Numbers in parentheses are the standard deviations

X-*Ray Single-crystal Analysis*.—The crystal of **(21)** was obtained by slow recrystallization from a saturated chloroform solution at room temperature. All data were collected at 23 °C on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation. The three standard reflections were remeasured periodically and showed no significant discrepancy. Table 4 summarizes the crystal data and the collection conditions for the benzo[*b*]thiin-4-one 1,1-dioxide **(21)**. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares procedure using the *X*-ray system program originated by Stewart.[17] Atom-scattering factors used were those listed in the International Tables for *X*-ray Crystallography.[18] Fourteen of the H atoms were located on different electron density maps following partial refinement. All H atoms were subsequently placed in calculated positions and assigned isotropic thermal parameters. The final cycle of refinement with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms afforded a value of 0.066 for the conventional index *R* on *F* for 2 000 reflections. The final different electron-density map contains no significant features.

Tables of final atomic parameters, anisotropic thermal parameters and selected bond angles are available from the Cambridge Crystallographic Data Centre.*

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* *Supplementary material:* see Instructions for Authors (1989), *J. Chem. Soc., Perkin Trans. 2*, 1989, January issue.

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