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Synthesis of 2-(Aminomethylene)-2H,3H-1-benzothiophene-3-one from 3-Bromo-4H-1-benzothiopyran-4-one as a New Donor-acceptor Chromophore

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2-(Amino-substituted methylene)-2H,3H-1-benzothiophene-3-ones were prepared by ring contraction of 3-bromo-4H-1-benzothiopyran-4-one with amines, as a new donor-acceptor chromophore. The structure of 2-(N,N-dimethylaminomethylene) derivative was determined by X-ray crystallographic analysis.

Nonlinear optical materials for shifting wavelength of a semiconductor laser to shorter wavelength are of interest in research on optical device technology. Organic compounds showing large nonlinearity must crystallize non-centrosymmetric form and have an intramolecular charge-transfer chromophore with a large quadratic hyperpolarizability β being responsible for second harmonic generation (SHG).1,2) Typical organic materials with large nonlinearity are anilino derivatives3) containing nitro groups as an acceptor, biphenyls,4) and chalcones.5)

We now found that 2-(aminomethylene)-2H,3H-1-benzothiophene-3-ones (**2**) which showed a new donor-acceptor chromophore applied to such materials were prepared by ring contraction of 4H-1-benzothiopyran-4-one (thiochromone) **1**. In this paper, we wish to report the preparation of **2**, an X-ray analysis of **2a**, and their SHG efficiencies.

Compound **2** was prepared from 3-bromo-thiochromone **1**6) as follows; Compound **1** was heated at 40 °C or reflux temperature for 24 h with methylamine, dimethylamine, or p-substituted aniline derivatives in ethanol. The mixture was poured into ice-water and the precipitate was filtered and chromatographed on silica gel using benzene-acetone (5:1) to give 2H,3H-1-benzothiophene-3-one derivative **2**, as an unexpected product (Table 1). Compounds **2a**-**2e** were recrystallized from ethanol, and compound **2a** was determined by X-ray crystallographic analysis. Other product isolated was thioindigo **3** (1-4% yield). In the ^{1}H NMR of **2b**-**2e**, the broad peak of the amino proton was observed at 10.6-12.4 ppm and assigned to typical intramolecular hydrogen bonding proton between O and NH proton. Thus, compounds **2b**-**2e** have cis-configuration in which the amino group and the carbonyl group are cis, while **2a** has trans-configuration as shown in Fig. 1. The structure of **2** was also supported by other spectral data.7) In reaction of **1** with p-nitroaniline or N,N-dimethylaniline, no 1-benzothiophene-3-one derivative was obtained.

Reaction of 2,3-dibromothiochromone 1,1-dioxide being sulfone derivative of the thiochromone with an amine generally gives 2-amino-substituted thiochromone 1,1-dioxides,9) but no ring contraction is observed. Though this ring contraction

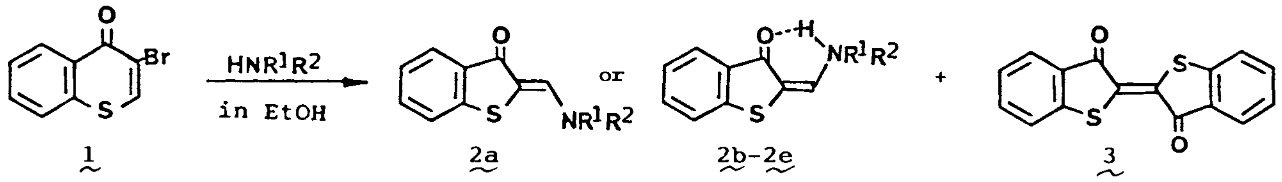

Table 1. Absorption maxima and the SHG efficiency of 2

Compd. No.	Substituent R^1	R^2	Yield/%	λ_{max}/nm (εx10^{-4})[a)]	SHG efficiency[b)]
2a	Me	Me	28	430 (1.53)	-[c)]
2b	H	Me	44	426 (1.21)	0.013
2c	H	C_6H_5	22	458 (2.14)	0.006
2d	H	p-Me-C_6H_4	37	558 (2.25)	0.018
2e	H	p-(OMe)-C_6H_4	39	457 (2.34)	7.0

a) In chloroform.

b) Measured by the powder method using the YAG laser (1064 nm). Values are relative intensities to urea.

c) SHG was not detected.

is analogous to the conversion of 3-chlorothioflavone to 2-benzoyl-2H,3H-1-benzothiophene-3-one[10)] by potassium hydroxide, a ring contraction of 3-bromothiochromone by amines in mild conditions has not been reported. This conversion of 1 to 2 may occur via a thiiranium intermediate[11)] or similar species.

The structure of 2a was solved by the direct method using the program MULTAN 78.[12,13)] All non-hydrogen atoms were refined anisotropically by the block-diagonal least-squares method and all hydrogen atoms were found from a difference Fourier map and refined isotropically.[14)] The final residual index, R, was 0.044. The structure of 2a together with several selected bond lengths is shown in Fig. 1.

The molecular frame including the aminomethylene group of 2a lies on a plane. Two molecular units along the a-axis are linked by a weak intermolecular hydrogen bond (2.54(3) Å) between a vinyl proton and Oa atom, the C9----Oa distance being 3.244 Å, as shown in Fig. 2.

A centrosymmetric arrangement of molecules in crystals is disadvantageous for development of the SHG efficiency. Though compound 2a involves the intramolecular donor-acceptor chromophore, it exhibits no SHG efficiency due to this molecular packing. On the other hand, replacement of N,N-dimethylamino group with secondary amino group results in SHG efficiency. These compounds are expected to make the the molecular arrangement without forming molecular aggregates by such intermolecular hydrogen bonds, because they have the cis-configulation. Compound 2e exhibited the 7.0-fold SHG efficiency, relative to that of urea. The absorption maxima of these compounds were in the range of 426-458 nm (Table 1), and they may overlap with second harmonic wavelength of semiconductor laser. Thus, they should be shifted to shorter wave lengths to apply to nonlinear materials for semiconductor laser device. As it makes possible to shift to shorter wavelengths by conversion of 2 into sulfone derivatives,[16)] they will be new potential nonlinear optical materials.

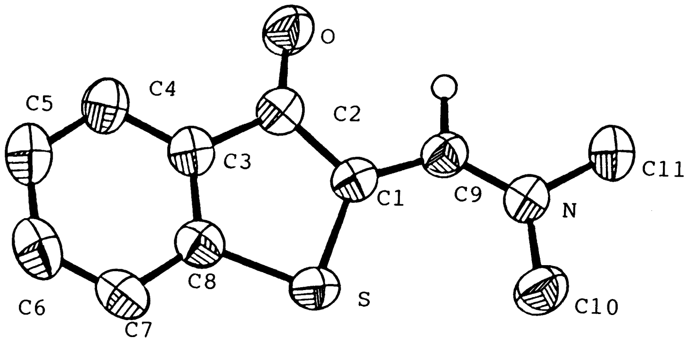

Fig. 1. ORTEP[15] drawing for 2a with atom numbering. Hydrogen atoms are omitted for clarity, except for H-C9.

Bond lengths (l/Å)	
S-C1	1.765(3)
S-C8	1.756(3)
C1-C2	1.448(4)
C2-C3	1.470(4)
C1-C9	1.376(4)
C2-O	1.237(4)
C9-N	1.324(4)

Bond angles (ϕ/°)	
C1-S-C8	90.9(1)
S-C1-C2	112.6(2)
C1-C2-O	126.1(3)
C1-C2-C3	109.7(2)
C2-C1-C9	118.5(2)
C1-C9-N	131.9(3)

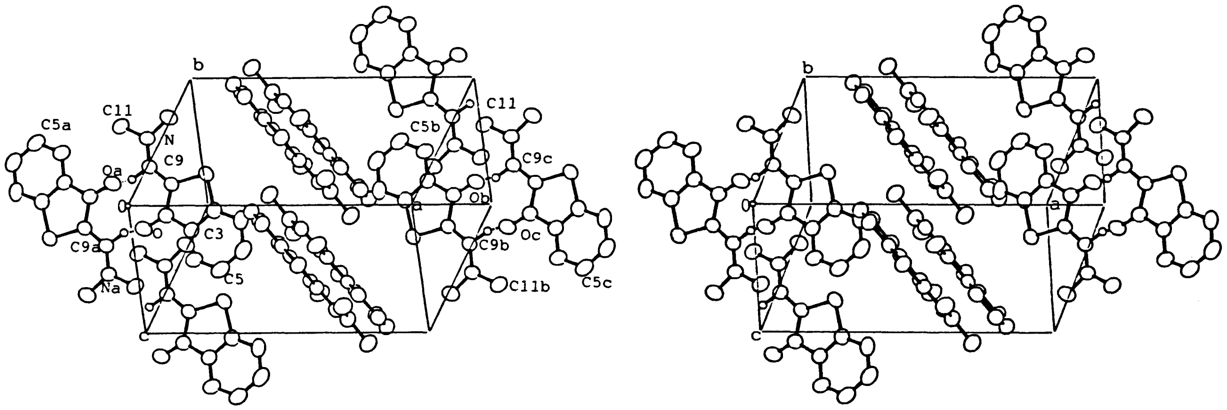

Fig. 2. Stereo drawing[15] for 2a in the unit cell. Symmetry code: a:-x,-y,-z, b: 1-x,1-y,1-z, c:1+x,1+y,1+z. C9---Oa, O---C9a, C9b---Oc, Ob---C9c: 3.244 Å.

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7) All new 1-benzothiophene-3-ones described here gave satisfactory elemental anal-

yses. Melting points were determined on a Rigaku TG-DSC calorimeter with 10 °C/min under nitrogen (100 ml/min). The spectral data and mp of 2 were as follows: 2a; mp 199.9 °C. ^{1}H NMR ($CDCl_3$) δ=3.34 (6H,s), 7.29 (1H,dt,J=1 and 7 Hz), 7.53 (1H,dt,J=1 and 7 Hz), 7.61 (1H,dd,J=1 and 8 Hz), 7.81 (1H,dd,J=1 and 8 Hz), 7.87 (1H,s). IR 1640 cm^{-1}(CO). MS m/z 205 (M^+,100), 190 (31), 175 (16), 162 (27). 2b; mp 186.7 °C. ^{1}H NMR ($CDCl_3$) δ=3.27 (3H,s), 7.29 (1H,t,J=7Hz), 7.51 (1H,dt,J=1 and 8 Hz), 7.64 (1H,d,J=8 Hz), 7.70 (1H,s), 7.83 (1H,d,J=8 Hz), 10.6 (1H,b). IR 3200 cm^{-1}(NH), 1650 cm^{-1}(CO), MS m/z 191(M^+;100), 176 (20), 162 (29). 2c; mp 178.7 °C. ^{1}H NMR ($CDCl_3$) δ=7.30-7.45 (6H,m), 7.60 (1H,dt,J=1 and 8 Hz), 7.71 (1H,dd,J=1 and 8 Hz), 7.91 (1H,dd,J=1 and 8 Hz), 8.40 (1H,s), 9.46 (b).8) IR 3200 cm^{-1}(NH), 1655 cm^{-1}(CO). MS m/z 253 (M^+;100), 236 (18). 2d; mp 196.2 °C. ^{1}H NMR ($CDCl_3$) δ=2.33 (3H,s), 7.25 (2H,d,J=6 Hz), 7.31 (2H,d,J=6 Hz), 7.35 (1H, dt,J=1 and 7 Hz), 7.58 (1H,dt,J=1 and 7 Hz), 7.70 (1H,dd,J=1 and 8 Hz), 7.90 (1H,dd,J=1 and 8 Hz), 8.40 (1H,s), 9.40 (b).8) IR 3220 cm^{-1}(NH), 1655 cm^{-1}(CO). MS m/z 267 (M^+, 100), 250 (20). 2e; mp 177.1 °C. ^{1}H NMR ($CDCl_3$) δ=3.82 (3H,s), 7.01 (2H,d, J= 9Hz), 7.32 (1H,dt,J=1 and 7 Hz), 7.38 (2H,d,J=9 Hz), 7.57 (1H,dt, J=1 and 7 Hz), 7.70 (1H, dd, J=1 and 7 Hz), 7.90 (1H,dd,J=1 and 8 Hz), 8.35 (1H, s), 9.37 (b).8) IR 3200 cm^{-1}(NH), 1650 cm^{-1}(CO), MS m/z 283 (M^+;100), 268 (38).

8) The broad peak at ca. 12.4 ppm was also observed with same intensity of the peak of ca. 9.40 ppm.

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12) A crystal of dimensions of 0.5x0.4x0.13 mm^3 of 2a for X-ray crystallographic analysis was obtained from a saturated solution of 2a in ethanol. The crystal data are as follows: FW=205.275, monoclinic, space group $P2_1/n$, a=14.007(7), b=9.369(4), c=7.519(2) Å, β=97.76(5)°, V=977.8 $Å^3$, D_{calcd}=1.39 g cm^{-3} and Z=4. X-ray diffraction intensities were collected in $2\theta \leq 55°$ on Rigaku AFC-6R diffractometer with Mo-Kα (λ=0.71 Å) radiation. A total of 2369 independent reflections were measured, of which 1405 reflections with $|F_o| > 3\sigma(|F_o|)$ were used for calculation.

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16) For example, 2-(Anilinomethylene)-2H,3H-1-benzothiophene-3-one 1,1-dioxide which was sulfone derivative of 2c absorbed at 381 nm.

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