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3-Aminoxanthene-9-one

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Abstract

3-Aminoxanthene-9-one, crystallized from ethanol solution, is non-centrosymmetric, belonging to the $P2_1$ space group. The crystal shows a large second harmonic generation (SHG) in laser radiation and a short cut-off wavelength for light absorption. There is a possibility that this crystal could be used as a material for an SHG device.

Comment

SHG devices of laser diodes are useful as compact blue lasers. Crystals of organic compounds containing a π-electron conjugated system with donors and acceptors have potential as SHG devices. But they are generally centrosymmetric, and they usually have absorptions in the visible light region even if they are non-centrosymmetric.

To solve this problem, we studied compounds with π-electron conjugated systems connected by a carbonyl group and an O atom, and found some showed large second harmonic generation and short cut-off wavelengths for light absorption (Imanishi, Itoh, Kakuta & Mukoh, 1990). The title compound is non-centrosymmetric, its second harmonic light intensity is 13 times that of urea, and its cut-off wavelength is 400 nm.

The crystal structure analysis was carried out in order to understand the effect of the crystal structure on SHG activity and the phase-match conditions. The crystal belongs to the $P2_1$ space group, and has two molecules per unit cell. Large dipole moments in these two molecules do not cancel each other and, therefore, the crystal produces a large second harmonic signal. When the b axis of the crystal is coincided with the optical y axis, the crystal has phase-match conditions in wide range of directions except in the y-axis direction.

When the crystal structure of the title compound is compared with that of xanthene-9-one (Biswast & Sen, 1982), it is found that the amino group substituted at C3 does not cause the title compound to be centrosymmetric, in spite of its properties as a strong donor, and enhances second harmonic activity sufficiently.

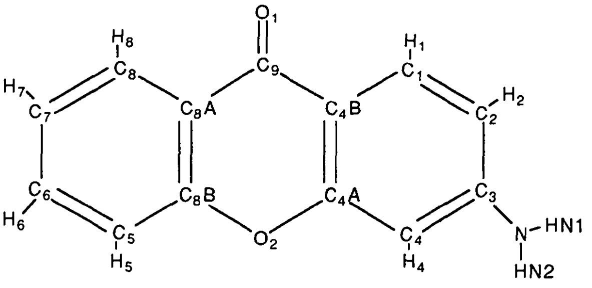

Fig. 1. Chemical structural diagram of 3-aminoxanthene-9-one.

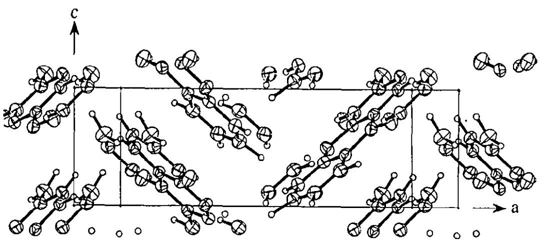

Fig. 2. Projection of the structure onto the *ac* plane.

Experimental

Crystal data

$C_{13}H_9NO_2$
M_r = 211.21
Monoclinic
$P2_1$
a = 13.394 (8) Å
b = 4.718 (2) Å
c = 8.084 (7) Å
β = 103.12 (2)°
V = 497.5 (5) Å^3
Z = 2
D_x = 1.41 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8–11°
μ = 0.090 mm^{-1}
T = 296 K
Plate
0.4 × 0.3 × 0.2 mm
Colourless

Data collection

Syntex *R*3 diffractometer
2θ-ω scans
Absorption correction: none
1276 measured reflections
1275 independent reflections
1116 observed reflections [$|F_o| > 3\sigma(|F_o|)$]
$\theta_{\max}$ = 27.5°

$h = 0 \rightarrow 17$
$k = 0 \rightarrow 6$
$l = -10 \rightarrow 10$
3 standard reflections monitored every 50 reflections intensity variation: 0.97–1.02%

Refinement

Refinement on F^2
$R = 0.043$
$wR = 0.056$
$S = 1.83$
1116 reflections
172 parameters
All H-atom parameters refined

$w = 1/\sigma(|F_o|)^2$
$(\Delta/\sigma)_{\max} = 0.18$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
O1	0.1758 (2)	0.2595	0.8055 (2)	4.96 (5)
O2	0.3085 (1)	0.4909 (8)	0.4162 (2)	4.19 (5)
N	0.0909 (2)	−0.1105 (1)	0.0262 (4)	5.15 (8)
C1	0.1078 (2)	0.0007 (9)	0.4770 (3)	3.64 (6)
C2	0.0787 (2)	−0.1050 (9)	0.3179 (4)	3.99 (7)
C3	0.1247 (2)	−0.0100 (9)	0.1873 (3)	3.71 (6)
C4	0.2024 (2)	0.1912 (1)	0.2261 (3)	3.98 (7)
C4*A*	0.2312 (2)	0.2954 (9)	0.3890 (3)	3.43 (6)
C4*B*	0.1847 (2)	0.2071 (9)	0.5192 (3)	3.35 (6)
C5	0.4186 (2)	0.8063 (1)	0.5927 (4)	4.42 (8)
C6	0.4525 (2)	0.9362 (1)	0.7464 (4)	4.75 (8)
C7	0.4094 (2)	0.8761 (1)	0.8821 (4)	4.74 (8)
C8	0.3316 (2)	0.6806 (9)	0.8636 (4)	4.22 (8)
C8*A*	0.2956 (2)	0.5418 (9)	0.7090 (3)	3.52 (6)
C8*B*	0.3395 (2)	0.6089 (9)	0.5733 (3)	3.55 (6)
C9	0.2153 (2)	0.3284 (9)	0.6868 (3)	3.57 (6)

Table 2. *Selected bond distances* (Å) *and angles* (°)

O1—C9	1.239 (3)	O2—C4*A*	1.366 (3)
O2—C8*B*	1.362 (3)	N—C3	1.363 (4)
C1—C2	1.352 (4)	C1—C4*B*	1.402 (4)
C2—C3	1.410 (4)	C3—C4	1.391 (4)
C4—C4*A*	1.376 (4)	C4*A*—C4*B*	1.403 (3)
C4*B*—C9	1.442 (3)	C5—C6	1.367 (4)
C5—C8*B*	1.392 (4)	C6—C7	1.380 (4)
C7—C8	1.374 (4)	C8—C8*A*	1.397 (4)
C8*A*—C8*B*	1.394 (4)	C8*A*—C9	1.454 (4)
C4*A*—O2—C8*B*	119.1 (2)	C2—C1—C4*B*	121.7 (3)
C1—C2—C3	121.0 (3)	N—C3—C2	119.9 (3)
N—C3—C4	121.5 (3)	C2—C3—C4	118.6 (3)
C3—C4—C4*A*	119.5 (3)	O2—C4*A*—C4	115.6 (2)
O2—C4*A*—C4*B*	121.9 (2)	C4—C4*A*—C4*B*	122.4 (2)
C1—C4*B*—C4*A*	116.8 (2)	C1—C4*B*—C9	122.7 (2)
C4*A*—C4*B*—C9	120.5 (2)	C6—C5—C8*B*	119.3 (3)
C5—C6—C7	121.2 (3)	C6—C7—C8	119.7 (3)
C7—C8—C8*A*	120.8 (3)	C8—C8*A*—C8*B*	118.4 (2)
C8—C8*A*—C9	122.0 (2)	C8*B*—C8*A*—C9	119.6 (2)
O2—C8*B*—C5	116.2 (2)	O2—C8*B*—C8*A*	123.1 (2)
C5—C8*B*—C8*A*	120.7 (3)	O1—C9—C4*B*	122.9 (2)
O1—C9—C8*A*	121.3 (2)	C4*B*—C9—C8*A*	115.8 (2)

Synthesis of the title compound was carried out by Friedel-Crafts reaction (Goldberg & Walker, 1953). The reaction mixture was purified by column chromatography on alumina and by heating with active charcoal in acetone. Single crystals suitable for X-ray diffraction were obtained from an ethanol solution by slow evaporation. Evaluation of SHG activity was carried out according to the technique of Kurtz & Perry (1968). Data were corrected for Lorentz and polarization effects in the usual way. Absorption corrections were not applied as the linear absorption coefficient was sufficiently small. The structure was solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least-squares refinement was performed with 16 anisotropic non-H atoms and nine isotropic H atoms. All calculations were carried out on a HITAC M-200H computer at Hiroshima University using the structure analysis program system *UNICS*3 (Sakurai & Kobayashi, 1979).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles including those involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71282 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1020]

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Verfeinerung der Kristallstruktur des Tetraethylammoniumheptaiodids†

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Abstract

The long known structure of tetraethylammonium heptaiodide, Et_4NI_7, has been largely confirmed. It consists of linear triiodide units I_3^- perpendicular to layers of iodine molecules I_2. They are connected to the ends of the I_3^- ions forming a network of zigzag chains. The holes of this iodine network are filled with the now ordered cations, so the centrosymmetric space group *Abam* has to be replaced by the noncentrosymmetric *Aba*2.

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† Untersuchungen an Polyhalogeniden. 10. Teil 9: Tebbe & Krauss (1990).

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