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3-Isopropyl-6,6-dimethyl-5-(1-naphthylamino)-1,2,4-trioxane

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Abstract. $C_{18}H_{23}NO_3$, monoclinic, $P2_1/c$, a = 10·061 (2), b = 9·117 (2), c = 18·027 (2) Å, β = 91·49 (2)°, $Z = 4$, $D_m = 1·19$, $D_x = 1·202$ g cm^{-3}. The torsion angle of the peroxide bond is only −68·4 (2)° and its length is 1·469 (2) Å. The exposed O—O bond may be easily cleaved by alkali in solution, which is a trigger for chemiluminescence of this compound.

Introduction. The title compound is a chemiluminescent substance which emits light in basic DMSO solution (Akutagawa, Aoyama, Omote & Yamamoto, 1976; Yamamoto, Aoyama, Omote, Akutagawa, Takenaka & Sasada, 1977). Crystals were obtained from an *n*-hexane solution. Density was measured by flotation. A crystal, 0·4 × 0·5 × 0·6 mm in size, was

Table 1. *Fractional atomic coordinates*

Standard deviations are in parentheses.

	x (×10^5)	y (×10^5)	z (×10^5)
N	34967 (18)	38148 (21)	34049 (11)
O(1)	53934 (16)	72129 (17)	32647 (10)
O(2)	66816 (15)	64858 (17)	31812 (9)
C(3)	67366 (23)	53930 (25)	37413 (13)
O(4)	57795 (14)	43191 (16)	35588 (8)
C(5)	44538 (23)	49090 (26)	35844 (13)
C(6)	43211 (24)	62132 (25)	30558 (14)
C(7)	81116 (24)	47362 (27)	37617 (14)
C(8)	91417 (27)	58719 (32)	40028 (18)
C(9)	81449 (26)	34396 (31)	42893 (17)
C(10)	43888 (26)	58080 (29)	22420 (15)
C(11)	31056 (27)	71239 (32)	32335 (18)
C(12)	32269 (22)	26837 (25)	39135 (13)
C(13)	39930 (23)	24142 (26)	45382 (13)
C(14)	36649 (25)	12926 (28)	50303 (14)
C(15)	26011 (26)	4168 (28)	48891 (15)
C(16)	17827 (23)	6484 (27)	42506 (14)
C(17)	6538 (26)	−2329 (29)	40908 (15)
C(18)	−1449 (26)	142 (33)	34908 (17)
C(19)	1271 (25)	11655 (34)	30177 (15)
C(20)	12050 (24)	20477 (30)	31462 (14)
C(21)	20745 (22)	18040 (26)	37614 (13)

	x (×10^4)	y (×10^4)	z (×10^4)
H(N)	3490 (19)	3542 (24)	2940 (11)
H(13)	4806 (17)	2955 (20)	4611 (10)
H(14)	4266 (19)	1141 (22)	5464 (11)
H(15)	2387 (20)	−367 (23)	5219 (11)
H(17)	504 (20)	−1065 (24)	4431 (12)
H(18)	−971 (21)	−629 (27)	3371 (13)
H(19)	−471 (21)	1496 (27)	2612 (13)
H(20)	1408 (18)	2841 (21)	2814 (10)
H(3)	6457 (17)	5861 (20)	4237 (10)
H(5)	4294 (17)	5247 (20)	4096 (10)
H(7)	8295 (17)	4384 (20)	3256 (10)
H(81)	9124 (22)	6727 (26)	3669 (13)
H(82)	10026 (24)	5432 (28)	4016 (14)
H(83)	8898 (23)	6272 (27)	4493 (13)
H(91)	7564 (23)	2646 (26)	4117 (13)
H(92)	7892 (22)	3845 (26)	4810 (13)
H(93)	9041 (23)	3031 (26)	4336 (13)
H(101)	3599 (21)	5238 (25)	2115 (12)
H(102)	5235 (24)	5258 (28)	2138 (13)
H(103)	4343 (21)	6754 (26)	1937 (12)
H(111)	2351 (24)	6515 (27)	3212 (14)
H(112)	3046 (25)	7942 (29)	2909 (15)
H(113)	3123 (24)	7469 (27)	3783 (14)

used for data collection on a Rigaku computer-controlled four-circle diffractometer, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). The cell parameters were determined by least-squares calculation with 35 high-angle reflexions. Intensities were measured in the ω–2θ scan mode with a scan width of 2° (in 2θ) plus α_1–α_2 divergence, at a scan speed of 8° (in 2θ) min^{-1}. Five reference reflexions, monitored after every 50 reflexions, showed no significant intensity variations throughout the data collection. Out of 2920 independent reflexions in the range $2 \le 2\theta \le 50°$, 984 weak reflexions with counts below background were considered zero-reflexions. The data were corrected for Lorentz and polarization factors but not for absorption effects ($\mu = 0{\cdot}95$ cm^{-1}).

The structure was solved by the direct method and its parameters were refined by block-diagonal least-squares techniques. All the H atoms, found on a difference map, were included. The quantity minimized was $\Sigma\, w(|F_o| - |F_c|)^2$, with $w = 1/(\sigma_p^2 + qF_o^2)$, where σ_p is due to counting statistics and q is $8{\cdot}44 \times 10^{-5}$, derived from the variation of the monitored reflexions. The zero-reflexions were included in the least-squares calculation by assuming $F_o = F_{\rm lim}$ and $w = w(F_{\rm lim})$, where $F_{\rm lim}$ is 6·537, an observational threshold value, but those for which $|F_c| < F_{\rm lim}$ were omitted. The final R_w $\{R_w = [\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, wF_o^2]^{1/2}\}$ was 0·043 and the conventional R was 0·086 ($R = 0{\cdot}063$ for $F_o \ge 3/\sqrt{w}$); the maximum shift of parameters in the last cycle was $0{\cdot}17\sigma$ for C, N, O and $0{\cdot}31\sigma$ for H atoms. Atomic parameters are listed in Table 1.* Bond distances and angles are given in Fig. 1.

Discussion. The conformation of the trioxane ring containing a peroxide bond has never been reported. The chair conformation of the ring results in a dihedral angle C(6)–O(1)–O(2)–C(3) of −68·4 (2)°. This angle is the smallest in comparison with those of several peroxides (81 to 180°) (Fritch, Christoph & Schaefer, 1973; Groth, 1969, 1975). The length of the peroxide

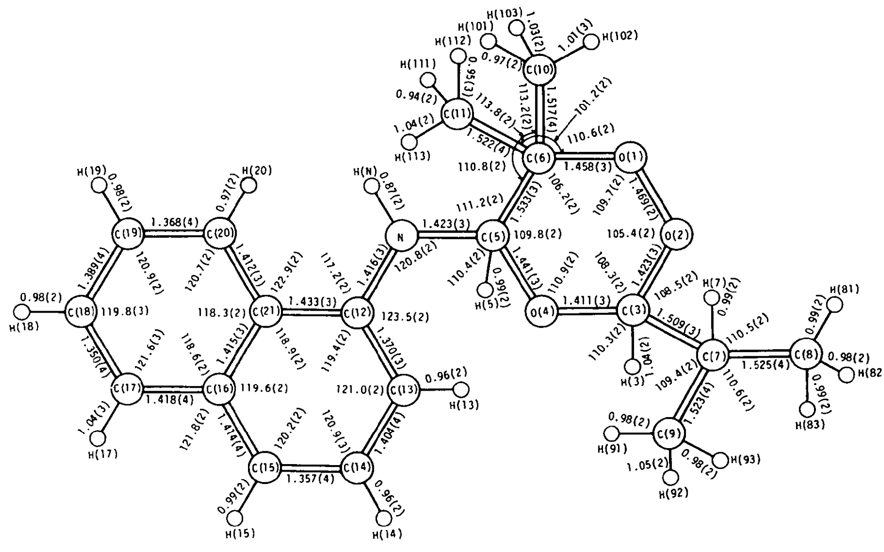

Fig. 1. Bond distances (Å) and bond angles (°), with their e.s.d.'s in parentheses.

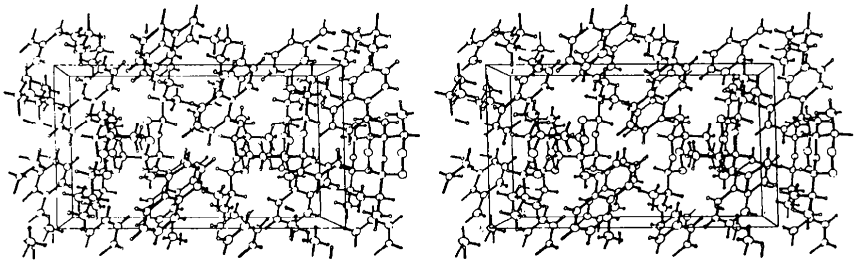

Fig. 2. Stereoscopic diagram showing the molecular packing viewed along **b**.

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* Lists of structure factors, the thermal parameters for all the atoms and the bond angles involving the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32825 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

bond, 1·469 (2) Å, is in the range found for the peroxides mentioned above. The isopropyl and the naphthylamino groups are bonded to the trioxane ring in equatorial positions. The naphthyl group is slightly twisted about the C(16)–C(21) bond. The bond lengths in the naphthyl ring are similar to those in 1,8-bis(dimethylamino)naphthalene (Einspahr, Robert, Marsh & Roberts, 1973). The two C–N distances and the C–N–C angle show that the N atom is in sp^2 hybridization. The dihedral angle between the plane C(5)–N–C(12) and the mean plane of the naphthylamino group is 12·0 (2)° by rotation about the C(12)–N bond. The torsion angles C(12)–N–C(5)–C(6) and C(12)–N–C(5)–O(4) are −165·1 (2) and 72·7 (3)°, respectively. Such a relative orientation of the bulky naphthylamino group and the trioxane ring could minimize the repulsions from H(5), O(4), and the two methyl groups at C(6). The C(sp^3)–C(sp^3) bond distances, 1·509–1·523 Å, are all shortened. The small expansion of the N–C(12)–C(13) angle and the resulting contraction of N–C(12)–C(21) are attributable to a repulsion between C(5) and C(13), their distance apart being 2·908 Å. The O(1)–O(2) bond is exposed relative to the molecule. This suggests that in solution the peroxide bond is susceptible to attack by alkali and its bond cleavage is a trigger for chemiluminescence.

As shown in Fig. 2, the molecules are packed by van der Waals interactions. No hydrogen bonds are formed; the shortest intermolecular N···O distance is 3·555 (3) Å.

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Mercury Ethylxanthate

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Abstract. $Hg(SSCOC_2H_5)_2$, monoclinic, $P2_1$, a = 9·904 (2), b = 6·903 (7), c = 9·104 (8) Å, β = 100·21 (3)°, Z = 2, D_m = 2·49, D_x = 2·40 g cm^{-3}, absorption coefficient μ(Mo $K\alpha$) = 136·49 cm^{-1}, final R = 0·058. Each Hg atom is surrounded tetrahedrally by four S atoms at distances of 2·313 (8), 2·505 (9), 2·749 (8) and 2·943 (10) Å. A distorted two-dimensional network of 16-membered rings, $[-Hg-S-C-S-]_4$, is formed parallel to the (100) plane.

Introduction. The crystals were grown as thin plates or rectangular tablets from carbon tetrachloride. Intensities were collected on an equi-inclination type diffractometer READ-1 (Sakurai, Ito & Iimura, 1970) with graphite-monochromated Mo $K\alpha$ radiation. The measurement was carried out in the ω-scan mode with a scan speed of 1° min^{-1}. 1180 independent reflexions with intensities larger than 2·5 times the standard deviations were obtained. A crystal elongated along **b** with a cross-section of 0·11 × 0·11 mm was used. Absorption correction by approximation to a cylinder (μr = 0·735) was applied. No extinction correction was applied. The structure was analysed by heavy-atom Fourier synthesis. The atomic scattering factors and dispersion effects were taken from *International Tables for X-ray Crystallography* (1974). After three cycles of block-diagonal anisotropic least-squares refinement, in which the weighting scheme 1 for $0 < |F_o| < 90$ and $(90/F_o)^2$ for $|F_o| \geq 90$ was chosen, the R value reduced