

Other articles discussing distortions related to the incipient nucleophilic attack of proximate nucleophiles on diazonium functionalities include reports by Gougoutas (1979, 1982), Wallis & Dunitz (1984) and Greenberg & Okaya (1969).

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#### References

- GABE, E. J., LE PAGE, Y., CHARLAND, J.-P., LEE, F. L. & WHITE, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- GLASER, R. (1989). *J. Phys. Chem.* **93**, 7993–8003.
- GLASER, R. (1990). *J. Comput. Chem.* **11**, 663–679.
- GLASER, R., CHOY, G. S.-C. & HALL, M. K. (1991). *J. Am. Chem. Soc.* **113**, 1109–1120.
- GLASER, R., HORAN, C. J., CHOY, G. S.-C. & HARRIS, B. (1992). *Phosphorus Sulfur Silicon*. In the press.
- GLASER, R., HORAN, C. J., NELSON, E. & HALL, M. K. (1992). *J. Org. Chem.* **57**, 215–228.
- GLASER, R. & STREITWIESER, A. (1987). *J. Am. Chem. Soc.* **109**, 1258–1260.
- GOUGOUTAS, J. Z. (1979). *J. Am. Chem. Soc.* **101**, 5672–5675.
- GOUGOUTAS, J. Z. (1982). *Cryst. Struct. Commun.* **11**, 1305–1310.
- GOUGOUTAS, J. Z. & JOHNSON, J. (1978). *J. Am. Chem. Soc.* **100**, 5816–5820.
- GREENBERG, B. & OKAYA, Y. (1969). *Acta Cryst.* **B25**, 2101–2108.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting crystal and molecular structures. Univ. of Cambridge, England.
- WALLIS, J. D. & DUNITZ, J. D. (1984). *J. Chem. Soc. Chem. Commun.* pp. 671–672.

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## Structure of an Organic Photochromic Compound. 6,7,8a,9-Tetrahydro-17,17-dimethylnaphtho[1'',2'':5',6'] [1,4]oxazino[3',2':2,3] [1,4]oxazino[4,3-a] [3H]indole

BY ANDREW TEH HU\* AND MING-SING WANG

*Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan 300*

AND SUE-LEIN WANG

*Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300*

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**Abstract.** Following the general procedure for the synthesis of spirooxazines, an unexpected new compound was obtained:  $C_{23}H_{22}N_2O_2$ ,  $M_r = 358.4$ , monoclinic,  $P2_1/n$ ,  $a = 13.215$  (3),  $b = 9.321$  (1),  $c = 15.600$  (4) Å,  $\beta = 105.68$  (2)°,  $V = 1850.0$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.287$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.077$  mm<sup>-1</sup>,  $F(000) = 760$ ,  $T = 296$  K, final  $R = 0.0389$ ,  $wR = 0.0415$  for 1775 reflections with  $I \geq 3.0\sigma(I)$ . This new compound, in chloroform solution, shows a colour change on irradiation with UV light or exposure to sunlight, and reverts to a light brown colour when kept in the dark after the removal of UV light.

**Introduction.** Organic photochromic compounds have attracted significant attention in view of their potential applications in optical memory devices, light filters, optical switches, actinometers, dec-

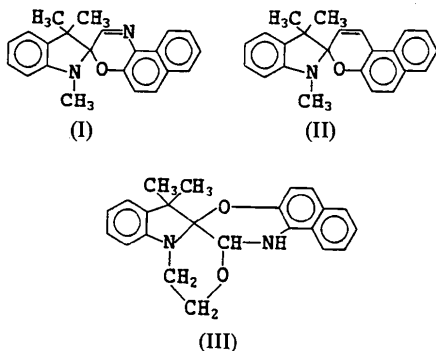
oration, *etc.* (Bertelson, 1971; Guglielmetti, Chu, Gauglitz, Ichimura, Michl, Wild, Renn, Hampp & Brauchle, 1990). Spirooxazines are important photochromic compounds because of their good fatigue resistance to light.

The chemical structure of the spirooxazine (I) (Millini, Del Piero, Allegrini, Crisci & Malatesta, 1991) is very similar to that of the spiropyran (II) (Kellmann, Tfibel, Dubest, Levoir, Aubard, Pottier & Guglielmetti, 1989), a photochromic compound of current interest. The only difference between (I) and (II) is that (I) has a C=N bond in place of the C=C bond in (II). On exposure to UV light, both undergo a colour change and the C(spiro)—O bond is cleaved heterolytically. The reverse colour change occurs when the irradiated form is exposed to visible light or heat.

In general, spirooxazines are directly synthesized by the reaction of an indoleninium salt with an *ortho*-nitroso aromatic alcohol (Nakamura & Tani-

\* To whom correspondence should be addressed.

guchi, 1991). In this study, we attempted to prepare the spirooxazine by this procedure but obtained an unexpected new compound (III), whose structure is established by X-ray analysis.



**Experimental.** Details of the synthetic work will be described elsewhere (Hu & Wang, 1992). Crystals were grown from chloroform/*n*-hexane. A colourless single crystal of dimensions 0.52 × 0.40 × 0.20 mm was mounted on a Siemens R3m/V diffractometer and data collected with graphite-monochromated Mo K $\alpha$  radiation and  $\theta/2\theta$  scans. The cell parameters were determined by least squares from 12 reflections with  $7.90 < 2\theta < 20.64^\circ$ . A total of 3646 reflections were collected, 1775 with  $I \geq 3.0\sigma(I)$ , to maximum  $2\theta = 50^\circ$  and for  $-15 \leq h \leq 15$ ,  $0 \leq k \leq 11$ ,  $0 \leq l \leq 17$ . No significant variation was observed in the intensities of three standards monitored every 50 reflections. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by full-matrix least squares based on  $F$ . All of the non-H atoms were refined with anisotropic temperature factors. All of the H atoms were located on a difference map and refined with isotropic temperature factors. At convergence,  $R = 0.0389$ ,  $wR = 0.0415$   $\{w = [\sigma^2(F) + 0.0008F^2]^{-1}$ ,  $\sigma^2(F)$  based on counting statistics},  $(\Delta/\sigma)_{\max} = 0.002$ ,  $S = 1.19$ ,  $(\Delta\rho)_{\max} = 0.15$ ,  $(\Delta\rho)_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$ . Scattering factors were taken from *International Tables for X-ray crystallography* (1974,

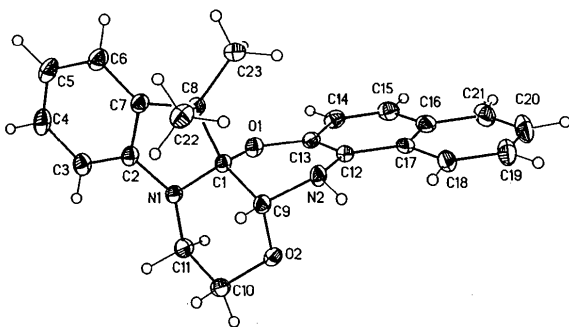


Fig. 1. Drawing of the title compound.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ )

Equivalent isotropic  $U$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
O(1)	6620 (1)	506 (2)	8584 (1)	48 (1)
O(2)	7990 (1)	2668 (2)	8229 (1)	47 (1)
N(1)	8370 (2)	-112 (2)	8799 (1)	42 (1)
N(2)	7193 (2)	3186 (2)	9352 (1)	44 (1)
C(1)	7680 (2)	742 (3)	9154 (2)	37 (1)
C(2)	8446 (2)	-1485 (3)	9157 (2)	42 (1)
C(3)	8827 (2)	-2725 (3)	8877 (2)	52 (1)
C(4)	8912 (2)	-3938 (3)	9412 (2)	61 (1)
C(5)	8613 (2)	-3912 (3)	10194 (2)	65 (1)
C(6)	8197 (2)	-2665 (3)	10455 (2)	57 (1)
C(7)	8113 (2)	-1451 (3)	9938 (2)	44 (1)
C(8)	7786 (2)	60 (3)	10094 (2)	44 (1)
C(9)	7959 (2)	2315 (3)	9114 (2)	38 (1)
C(10)	8755 (2)	1841 (3)	7947 (2)	52 (1)
C(11)	8485 (2)	266 (3)	7925 (2)	48 (1)
C(12)	6148 (2)	2920 (3)	8873 (2)	40 (1)
C(13)	5892 (2)	1577 (3)	8520 (2)	43 (1)
C(14)	4850 (2)	1246 (3)	8057 (2)	55 (1)
C(15)	4083 (2)	2251 (4)	7964 (2)	61 (1)
C(16)	4311 (2)	3645 (3)	8316 (2)	54 (1)
C(17)	5359 (2)	3989 (3)	8782 (2)	44 (1)
C(18)	5580 (2)	5405 (3)	9111 (2)	55 (1)
C(19)	4801 (3)	6401 (4)	9004 (2)	71 (1)
C(20)	3768 (3)	6058 (4)	8563 (2)	82 (2)
C(21)	3525 (2)	4718 (4)	8235 (2)	69 (1)
C(22)	8685 (2)	759 (3)	10802 (2)	59 (1)
C(23)	6777 (2)	120 (3)	10389 (2)	66 (1)

Table 2. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

O(1)—C(1)	1.459 (3)	O(1)—C(13)	1.371 (3)
O(2)—C(9)	1.431 (3)	O(2)—C(10)	1.432 (4)
N(1)—C(1)	1.429 (3)	N(1)—C(2)	1.389 (3)
N(1)—C(11)	1.456 (3)	N(2)—C(9)	1.424 (3)
N(2)—C(12)	1.403 (3)	C(1)—C(8)	1.569 (3)
C(1)—C(9)	1.517 (3)	C(2)—C(3)	1.378 (4)
C(2)—C(7)	1.404 (4)	C(3)—C(4)	1.392 (4)
C(4)—C(5)	1.380 (5)	C(5)—C(6)	1.393 (4)
C(6)—C(7)	1.377 (4)	C(7)—C(8)	1.512 (4)
C(8)—C(22)	1.532 (3)	C(8)—C(23)	1.525 (4)
C(10)—C(11)	1.509 (4)	C(12)—C(13)	1.372 (4)
C(12)—C(17)	1.421 (4)	C(13)—C(14)	1.405 (3)
C(14)—C(15)	1.359 (4)	C(15)—C(16)	1.411 (5)
C(16)—C(17)	1.417 (3)	C(16)—C(21)	1.422 (5)
C(17)—C(18)	1.417 (4)	C(18)—C(19)	1.363 (4)
C(19)—C(20)	1.390 (5)	C(20)—C(21)	1.356 (6)
C(1)—O(1)—C(13)	118.3 (2)	C(9)—O(2)—C(10)	112.3 (2)
C(1)—N(1)—C(2)	110.0 (2)	C(1)—N(1)—C(11)	117.8 (2)
C(2)—N(1)—C(11)	125.8 (2)	C(9)—N(2)—C(12)	115.3 (2)
O(1)—C(1)—N(1)	106.7 (2)	O(1)—C(1)—C(8)	109.7 (2)
N(1)—C(1)—C(8)	103.4 (2)	O(1)—C(1)—C(9)	108.9 (2)
N(1)—C(1)—C(9)	109.6 (2)	C(8)—C(1)—C(9)	117.9 (2)
N(1)—C(2)—C(3)	129.7 (3)	N(1)—C(2)—C(7)	108.8 (2)
C(3)—C(2)—C(7)	121.4 (2)	C(2)—C(3)—C(4)	117.9 (3)
C(3)—C(4)—C(5)	121.3 (3)	C(4)—C(5)—C(6)	120.2 (3)
C(5)—C(6)—C(7)	119.3 (3)	C(2)—C(7)—C(6)	119.7 (2)
C(2)—C(7)—C(8)	109.3 (2)	C(6)—C(7)—C(8)	130.8 (3)
C(1)—C(8)—C(7)	100.6 (2)	C(1)—C(8)—C(22)	111.0 (2)
C(7)—C(8)—C(22)	108.2 (2)	C(1)—C(8)—C(23)	113.8 (2)
C(7)—C(8)—C(23)	113.2 (2)	C(22)—C(8)—C(23)	109.7 (2)
O(2)—C(9)—N(2)	109.2 (2)	O(2)—C(9)—C(1)	109.4 (2)
N(2)—C(9)—C(1)	110.0 (2)	O(2)—C(10)—C(11)	110.4 (2)
N(1)—C(11)—C(10)	107.3 (2)	N(2)—C(12)—C(13)	118.4 (2)
N(2)—C(12)—C(17)	121.2 (2)	C(13)—C(12)—C(17)	120.3 (2)
O(1)—C(1)—C(12)	122.9 (2)	O(1)—C(13)—C(14)	116.6 (2)
C(12)—C(13)—C(14)	120.5 (2)	C(13)—C(14)—C(15)	120.2 (3)
C(14)—C(15)—C(16)	121.2 (2)	C(15)—C(16)—C(17)	119.0 (3)
C(15)—C(16)—C(21)	122.6 (3)	C(17)—C(16)—C(21)	118.4 (3)
C(12)—C(17)—C(16)	118.8 (2)	C(12)—C(17)—C(18)	122.9 (2)
C(16)—C(17)—C(18)	118.3 (2)	C(17)—C(18)—C(19)	121.0 (2)
C(18)—C(19)—C(20)	120.8 (3)	C(19)—C(20)—C(21)	120.0 (3)
C(16)—C(21)—C(20)	121.4 (3)		

Vol. IV). All calculations were performed on a DEC MicroVAX II computer system using the *SHELXTL-Plus* programs (Sheldrick, 1990).

**Discussion.** The molecular structure and atomic labelling scheme are shown in Fig. 1. Atomic coordinates for all non-H atoms are given in Table 1,\* and the bond lengths and angles are listed in Table 2.

The structure of compound (III) is very similar to those of (I) and (II). In (I) and (II), the spiro atom is shared by two rings and displays regular  $sp^3$  hybridization, but in (III) three rings share the spiro atom. The dihedral angle between planes through O(1)—C(1)—C(9) and N(1)—C(1)—C(8) is  $88.6^\circ$ , similar to the angles in spirooxazines and spiropyrans [ $86.4$ – $89.6^\circ$  (Clegg, Norman, Flood, Sallans, Kwak, Kwiatkowski & Lasch, 1991)]. The dihedral angle between planes N(1)—C(1)—C(8) and N(1)—C(1)—C(9) is  $53.4^\circ$  and between planes N(1)—C(1)—C(9) and O(1)—C(1)—C(9) is  $23.6^\circ$ . The C(9)—N(2) bond of compound (III) is a single bond of length  $1.424 \text{ \AA}$ , clearly different from the C=N double bond,  $1.267 \text{ \AA}$ , in spirooxazine (Millini, Del Piero, Alle-

grini, Crisci & Malatesta, 1991). Other distances are comparable to those in (I) and (II).

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#### References

\* Lists of structure factors, anisotropic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55629 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1012]

- BERTELSON, R. C. (1971). *Photochromism*, edited by G. H. BROWN, pp. 733–840. New York: Wiley-Interscience.
- CLEGG, W., NORMAN, N. C., FLOOD, T., SALLANS, L., KWAK, W. S., KWIAKOWSKI, P. L. & LASCH, J. G. (1991). *Acta Cryst. C47*, 817–824.
- GUGLIEMMETTI, R., CHU, N. Y. C., GAUGLITZ, G., ICHIMURA, K., MICHL, J., WILD, U. P., RENN, A., HAMPP, N. & BRAUCHLE, C. (1990). *Photochromism: Molecules and Systems*, edited by H. DURR & H. BOUAS-LAURENT, pp. 854–975. Amsterdam: Elsevier.
- HU, A. T. & WANG, M.-S. (1992). In preparation.
- KELLMANN, A., TFIHEL, F., DUBEST, R., LEVOIR, P., AUBARD, J., POTTIER, E. & GUGLIEMMETTI, R. (1989). *J. Photochem. Photo-biol. A*, **49**, 63–73.
- MILLINI, R., DEL PIERO, G., ALLEGRINI, P., CRISCI, L. & MALATESTA, V. (1991). *Acta Cryst. C47*, 2567–2569.
- NAKAMURA, M. & TANIGUCHI, T. (1991). *J. Syn. Org. Chem. Jpn*, **49**, 392–402.
- SHELDRIK, G. M. (1990). *SHELXTL-Plus*. Version 4. Siemens X-ray Analytical Instruments, Inc., Madison, Wisconsin, USA.

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## Determination of the Stereochemistry of Oxandran-3-one; a Novel Methyltriterpene from *Oxandra asbeckii* (Annonaceae)

BY WINSTON F. TINTO\* AND LYNN C. BLAIR

*Centre for Natural Products Chemistry, University of Guyana, Georgetown, Guyana*

AND ALAN J. LOUGH, STEWART MCLEAN AND WILLIAM F. REYNOLDS†

*Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1*

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**Abstract.** (24*R*)-24-Methyl-21,24-oxylanost-9(11)-en-3-one,  $C_{31}H_{50}O_2$ ,  $M_r = 454.7$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.135$  (3),  $b = 17.639$  (4),  $c = 21.454$  (7)  $\text{\AA}$ ,  $V = 2700.1$  (16)  $\text{\AA}^3$ ,  $Z = 4$ ,  $D_x = 1.12 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.70930 \text{ \AA}$ ,  $\mu = 0.6 \text{ cm}^{-1}$ ,  $F(000) = 1008$ , room temperature,  $R = 0.052$  for 1519 observed reflections. The structure of oxandran-3-one, a methyltriterpene

with a novel skeletal structure, has been determined and shown to have the lanostane stereochemistry. There are some apparent distortions of bond lengths and angles in the molecule. C(4)—C(5) and C(16)—C(14) bonds are longer than normal, reflecting ring strain. C(25)—C(26) is apparently anomalously short but this is likely an artefact owing to libration about the C(17)—C(20) and/or C(24)—C(25) bonds.

\* Present address: Department of Chemistry, University of the West Indies (Cave Hill Campus), Bridgetown, Barbados.

† Author to whom correspondence should be addressed.

**Introduction.** As part of a continuing investigation of natural products isolated from Guyanese plant