

The Structure of a 1,3-Oxazonine Derivative Obtained by
Photochemical Addition of 6-Cyanophenanthridine
N-Oxide and 2,3-Dimethyl-2-butene

R. Oberti

Istituto di Cristallografia, via Bassi 6,
27100 Pavia, Italy

A. Albini and E. Fasani

Istituto di Chimica Organica, via Taramelli 10,
27100 Pavia, Italy

Received December 28, 1982

The crystal structure of 5,6-dihydro-5,5,6,6-tetramethyl-8-cyanodibenzo[*d,f*]1,3-oxazonine, obtained from the photochemical addition of 6-cyanophenanthridine *N*-oxide and 2,3-dimethyl-2-butene, is described.

J. Heterocyclic Chem., **20**, 1007 (1983).

Introduction.

Molecular rearrangement and/or de-oxygenation are the chemical consequences of the irradiation of six-membered heterocyclic *N*-oxides [1]. Ring-enlargement is often observed in an aprotic solvent. This is the case for 6-cyanophenanthridine *N*-oxide (**1**), which is reported to rearrange photochemically to compound **2** (yield *ca.* 78% in acetone or benzene) [2]. We found that in the presence of 0.1 *M* 2,3-dimethyl-2-butene the photochemical reaction of the *N*-oxide **1** takes a completely different course, the oxazepine **2** being formed only in traces, while the main product is a new compound **3** (35% yield). This is shown by elemental analysis to be a 1:1 adduct between **1** and the alkene, but the data from spectroscopic analysis (*e.g.* four different methyl groups are observed in nmr, the CN group absorption is practically undetectable in the ir) are not suf-

ficient for an unambiguous structure assignment. Therefore a crystallographic study was undertaken.

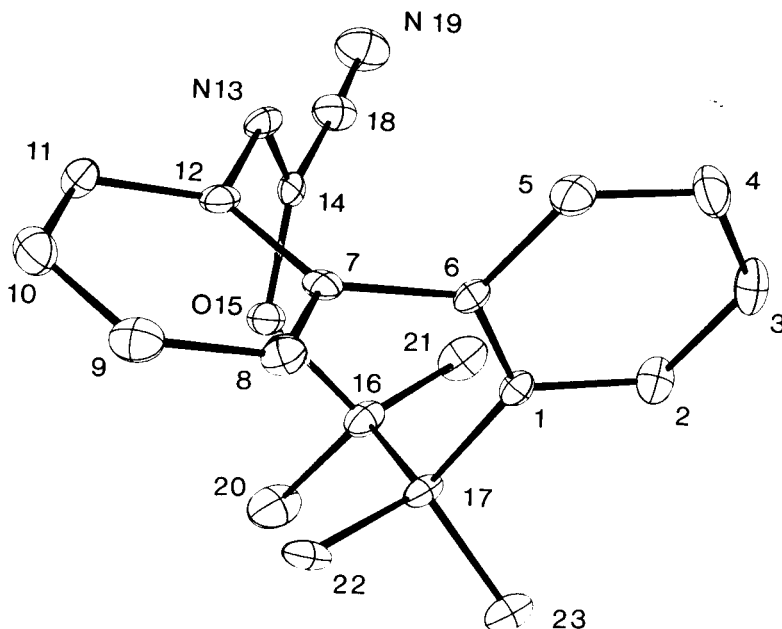
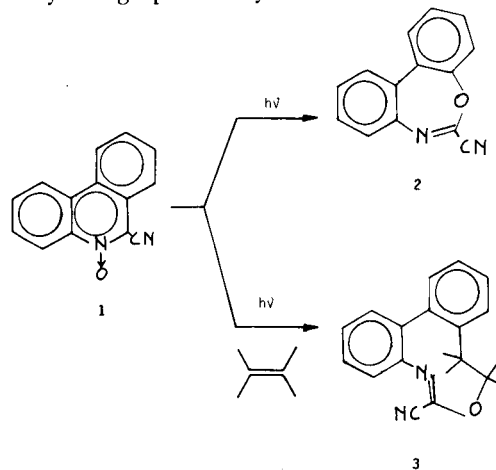


Figure. A perspective view of molecule **3** with the numbering scheme.

Table I

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters for the Non-hydrogen Atoms (E.s.d.'s are in parentheses)

$$B_{\text{eq}} = 4/3 E_i E_j \beta_i \beta_j a_i a_j$$

Atom	x/a	y/b	z/c	$B_{\text{eq}}(\text{\AA}^2)$
C1	4474(2)	4168(4)	6625(3)	2.9(1)
C2	4225(3)	5570(4)	6634(4)	3.7(1)
C3	4636(3)	6540(4)	7412(4)	4.5(1)
C4	5314(3)	6124(5)	8210(4)	4.6(2)
C5	5599(3)	4771(5)	8218(3)	3.9(1)
C6	5195(2)	3765(4)	7435(3)	2.7(1)
C7	5601(2)	2354(4)	7582(3)	2.6(1)
C8	6353(3)	2029(4)	7067(3)	3.5(1)
C9	6767(3)	745(5)	7243(4)	4.1(1)
C10	6438(3)	-218(5)	7945(4)	4.3(1)
C11	5716(3)	91(4)	8505(3)	3.8(1)
C12	5289(3)	1366(4)	8302(3)	2.9(1)
N13	4583(2)	1724(3)	8936(2)	3.1(1)
C14	3820(3)	1923(4)	8377(3)	3.0(1)
O15	3578(2)	1587(3)	7264(2)	3.4(1)
C16	3147(3)	2534(5)	6322(3)	3.5(1)
C17	3934(2)	3173(4)	5751(3)	3.1(1)
C18	3130(3)	2342(5)	9069(4)	3.9(1)
N19	2620(3)	2633(5)	9664(3)	5.8(1)
C20	2588(3)	1510(5)	5542(4)	5.5(1)
C21	2557(3)	3588(5)	6795(4)	4.8(1)
C22	4505(3)	2022(5)	5310(3)	4.0(1)
C23	3540(3)	3996(5)	4647(3)	4.5(1)

Table II

Bond Distances (\AA) for Non-hydrogen Atoms
(Standard Deviations are in Parentheses)

C1—C2	1.399(6)	C11—C12	1.392(5)
C1—C6	1.405(5)	C12—N13	1.422(5)
C1—C17	1.552(5)	N13—C14	1.269(5)
C2—C3	1.391(6)	C14—O15	1.341(4)
C3—C4	1.356(6)	C14—C18	1.461(6)
C4—C5	1.369(6)	O15—C16	1.508(5)
C5—C6	1.413(5)	C16—C17	1.568(5)
C6—C7	1.489(5)	C16—C20	1.521(6)
C7—C8	1.395(5)	C16—C21	1.504(6)
C7—C12	1.390(5)	C17—C22	1.535(5)
C8—C9	1.387(6)	C17—C23	1.561(5)
C9—C10	1.371(6)	C18—N19	1.139(5)
C10—C11	1.380(6)		

EXPERIMENTAL

Synthesis of Compound **3**.

In a flask 200 mg of the *N*-oxide **1** was dissolved in 200 ml of benzene, the solution was made 0.1 *M* in 2,3-dimethyl-2-butene and the solution was irradiated by means of a Pyrex filtered mercury arc at room temperature. Evaporation of the solvent and chromatography of the residue afforded product **3** in 35% yield. Crystallization from cyclohexane gave colourless crystals, mp 155–156°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}$: C, 78.92; H, 6.62; N, 9.20. Found: C, 79.10; H, 6.65; N, 9.21.

Crystal Data: $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}$, *mw* = 304.38. Monoclinic, space group $P2_1/n$: *a* = 15.208 (1); *b* = 9.604 (1); *c* = 11.650 (1); \AA , β = 97.46 (3)°; *Z* = 4.

Table III

Bond Angles (°) for Non-hydrogen Atoms
(Standard Deviations are in Parentheses)

C2—C1—C6	116.7(4)	C11—C12—N13	119.4(4)
C2—C1—C17	118.4(3)	C12—N13—C14	118.1(3)
C6—C1—C17	124.9(3)	N13—C14—O15	125.3(3)
C1—C2—C3	123.3(4)	N13—C14—C18	115.7(4)
C2—C3—C4	119.2(4)	O15—C14—C18	118.2(4)
C3—C4—C5	119.7(4)	C14—O15—C16	126.7(3)
C4—C5—C6	122.3(4)	O15—C16—C17	105.1(3)
C1—C6—C5	118.7(4)	O15—C16—C20	101.6(3)
C1—C6—C7	127.1(3)	O15—C16—C21	111.2(3)
C5—C6—C7	114.2(3)	C17—C16—C20	113.5(3)
C6—C7—C8	120.4(3)	C17—C16—C21	114.6(4)
C6—C7—C12	121.4(3)	C20—C16—C21	109.9(4)
C8—C7—C12	118.0(4)	C1—C17—C16	109.3(3)
C7—C8—C9	121.2(4)	C1—C17—C22	112.9(3)
C8—C9—C10	119.6(4)	C1—C17—C23	110.1(3)
C9—C10—C11	120.8(4)	C16—C17—C22	110.9(3)
C10—C11—C12	119.4(4)	C16—C17—C23	108.4(3)
C7—C12—C11	121.0(4)	C22—C17—C23	105.2(3)
C7—C12—N13	119.3(4)	C14—C18—N19	175.9(5)

Table IV

Thermal Parameters ($\times 10^4$) for Non-hydrogen Atoms
The Anisotropic Temperature Factor is of the Form:
 $\exp(-h^2\beta_{11} + \dots + hk\beta_{12} + \dots)$
(Standard Deviations in Parentheses)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C1	32(2)	79(6)	57(4)	-2(3)	11(2)	12(4)
C2	28(2)	92(6)	92(4)	-4(3)	-2(2)	13(4)
C3	49(3)	71(6)	125(5)	8(3)	15(3)	6(5)
C4	56(3)	86(7)	99(5)	-10(4)	0(3)	-15(5)
C5	44(3)	108(7)	65(4)	-9(3)	-12(2)	6(4)
C6	28(2)	84(6)	46(3)	-4(3)	8(2)	16(4)
C7	27(2)	87(6)	39(3)	2(3)	-2(2)	-3(4)
C8	38(2)	103(7)	60(4)	3(3)	2(2)	11(4)
C9	38(2)	146(7)	66(4)	7(4)	4(2)	-3(5)
C10	49(3)	110(7)	78(4)	21(4)	-5(3)	-7(5)
C11	55(3)	84(6)	58(4)	2(3)	1(3)	14(4)
C12	38(2)	89(6)	35(3)	-3(3)	0(2)	1(4)
N13	37(2)	96(5)	45(3)	-10(3)	9(2)	13(3)
C14	46(3)	72(5)	47(4)	-15(3)	16(3)	2(4)
O15	44(1)	94(4)	51(3)	-10(2)	6(1)	-1(3)
C16	35(2)	108(6)	57(4)	-13(3)	-4(2)	14(4)
C17	35(2)	97(6)	47(3)	-6(3)	0(2)	15(4)
C18	42(3)	128(7)	61(4)	-17(3)	7(3)	-9(4)
N19	59(3)	206(7)	88(4)	-6(4)	29(3)	-15(4)
C20	57(3)	181(8)	81(4)	-43(4)	-13(3)	11(5)
C21	34(2)	172(8)	94(4)	4(4)	15(3)	28(5)
C22	49(3)	136(7)	44(3)	-11(3)	3(2)	-13(4)
C23	51(3)	147(7)	65(4)	-1(3)	3(2)	29(4)

Structure Determination and Refinement.

X-Ray data collection was performed on a Philips 1100-four-circle computer-controlled diffractometer; the $\text{CuK}\alpha$ graphite monochromatized radiation ($\lambda = 1.5418 \text{ \AA}$) was used. Intensity measurements were made with the $\omega/2\theta$ scan technique in the θ range 32–50°, yielding the 1724 independent reflections; no equivalent monoclinic reflections were collected. Intensities were corrected for Lorentz and polarisation factors and then for absorption following the semi-empirical method of North *et al.* [3]. Only the 1168 reflections with $I > 3\sigma(I)$ were regarded as observed in the following calculations.

The structure was solved by direct method using the MULTAN 78 [4] computer system. Three cycles of isotropic full-matrix least-squares refinement were then carried out for the non-hydrogen atoms; also the secondary extinction coefficient was allowed to vary [5]. The atomic coordinates of the hydrogen atoms were then calculated on the basis of geometrical considerations and checked on a difference Fourier map. After three cycles of anisotropic refinement in which they were inserted but not allowed to vary, more accurate coordinates were calculated for the hydrogen atoms. Another two cycles of anisotropic refinement brought the conventional R index to 4.8%. The final value of the secondary extinction coefficient was 184.9×10^5 . The scattering factors used were those listed in the International Tables for X-ray Crystallography [6] for neutral atoms. Positional and thermal parameters for non-hydrogen atoms as well as bond distances and angles are reported in Tables I-IV. Lists of observed and calculated structure factors and of anisotropic temperature factors are available on request.

Discussion.

Quite surprisingly, compound **3** is shown to be 5,6-dihydro-5,5,6,6-tetramethyl-8-cyanodibenzo[*d,f*][1,3]oxazone. Thus, the photochemical reaction involves cleavage of the heterocyclic ring, shift of the oxygen atom from the nitrogen to the neighboring carbon and addition across the double bond. There is no previous evidence for this kind of photoreaction.

The dihydrooxoxazonine ring is folded and there is no conjugation between the three double bonds: the two benzene rings form an angle of 86.6° and the plane of the $-\text{N}=\text{C}(\text{CN})-\text{O}-$ function and the vicinal benzene ring form an angle of 72.3° .

The C(14)—N(13) and the C(14)—O(15) distances are 1.269 and 1.341 Å with a N(13)—C(14)—O(15) angle of 125.3° . These values are normal and can be compared with the values of 1.279 and 1.377 Å and 126.8° found in the case of a dihydro-1,3-oxazine [7]. A strong ir absorption

observed at 1625 cm^{-1} is attributed to the $-\text{N}=\text{C}(\text{R})-\text{O}-$ function and is at the lower limit of the values reported for open-chain imidates [8]. In the oxazepine **2** the corresponding ir absorption is observed at 1648 cm^{-1} . No oxazonine derivative had been crystallographically characterized as yet, nor indeed any oxonin derivative. The aromaticity of fully unsaturated oxonin has been discussed both from the theoretical point of view and on the basis of spectroscopic evidences [9]. The structure of compound **3**, a suitable model for 2,3-dihydrooxonin can be of interest for comparison.

Acknowledgment.

This work was supported in part by the Ministry of Education.

REFERENCES AND NOTES

- [1a] G. G. Spence, E. C. Taylor and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970); [b] F. Bellamy and J. Streith, *Heterocycles*, **4**, 1391 (1976).
- [2] C. Kaneko, R. Hayashi, M. Yamamori, K. Tokumura and M. Itoh, *Chem. Pharm. Bull.*, **26**, 2608 (1978).
- [3] A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Cryst.*, **A24**, 351 (1968).
- [4] F. Main and S. E. Hull, G. Germain, J. P. Declercq and M. M. Woolfson, "Solution of Crystal Structures from X-Ray Diffraction Data", Universities of York and Louvain.
- [5] P. Coppens and W. C. Hamilton, *Acta Cryst.*, **A26**, 71 (1970).
- [6] "International Tables for X-Ray Crystallography", Vol IV, Kynoch Press, Birmingham, England, 1974, p 99.
- [7] F. Garbani and L. Giarda, *Acta Cryst.*, **B29**, 1190 (1972).
- [8] G. Häfelinger in "The Chemistry of Amidines and Imidates", S. Patai, ed, J. Wiley and Sons, London, 1975, p 1.
- [9a] B. A. Hess, L. Schaad and C. W. Holyoke, *J. Am. Chem. Soc.*, **94**, 3657 (1972); [b] J. Aichara, *ibid.*, **98**, 2750 (1976); [c] A. G. Anastassiou and E. Reichmanis, *ibid.*, **98**, 8266 (1976) and references cited therein.