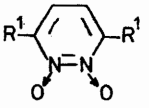
Correction to the Structure of the Photo-isomers of Pyridazine 1,2-Dioxides; *X*-Ray Crystal Structure Analysis

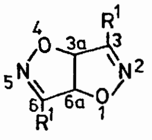
By Heihachiro Arai, Akio Ohsawa, Katsunori Saiki, Hiroshi Igeta,* Akio Tsuji, and Toshio Akimoto
(*School of Pharmacautical Sciences, Showa University, Shinagawa-ku, Tokyo* 142, *Japan*)
and Yoichi Iitaka
(*Faculty of Pharmaceutical Sciences, University of Tokyo, Bunkyo-ku, Tokyo* 113, *Japan*)

Summary The 1,4,6,7-dioxadiazocin structure (**3**), which was originally assigned to the photo-isomers of pyridazine 1,2-dioxide (**1**), is incorrect; chemical data and *X*-ray analysis show the correct structure to be 3a,6a-dihydroisoxazolo[5,4-*d*]isoxazole (**2**).

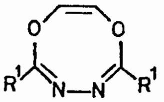
In a previous paper[1] we assigned the 1,4,6,7-dioxadiazocin structures (**3**) to the photo-isomers of pyridazine 1,2-dioxides (**1**). However, we have now found that the ^{1}H-n.m.r. data of the reduced products (**4**) from the photo-isomers and of their acetates (**5**) are inconsistent with the corresponding structures derived from the assumed structure (**3**).

The photo-isomer (**2a**) obtained from (**1a**) was treated with $NaBH_4$ in EtOH–tetrahydrofuran(THF) (1:5) at 0—5 °C to give a dihydro compound [(**4a**); oil, yield 10%]. Its n.m.r. spectrum showed geminally coupled signals at δ 3·18 (1H, dd, *J* 13·6 and 3·6 Hz, 3-H) and 3·56 (1H, br.d, *J* 13·6 Hz, 3-H′), an NH signal at 5·15 (1H, br.s), a signal at 5·35 (1H, dd, *J* 6·4 and 3·6 Hz, 3a-H) coupled with that of 3-H (*J* 3·6 Hz) and 6a-H at 5·67(1H, br.d, *J* 6·4 Hz), and a signal at 7·22 (1H, br.s, 6-H). The n.m.r. spectrum of the


(1)



(2)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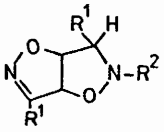
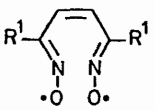

(4) R^2= H
(5) R^2= COMe

a: R^1 = H
b: R^1 = Me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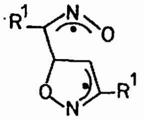
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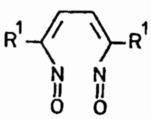
(8)

acetate [(**5a**); m.p. 104—105 °C, ν(C=O) 1670 cm^{-1} (KBr), yield 95%] obtained from (**4a**) with Ac_2O exhibited signals at δ 2·10 (3H, s, COMe), 3·38 (1H, dd, *J* 13·0 and 4·0 Hz, 3-H), 4·68 (1H, br.d, *J* 13·0 Hz, 3-H′), 5·38 (1H, dd, *J* 7·0 and 4·0 Hz, 3a-H), 5·74 (1H, br.d, *J* 7·0 Hz, 6a-H), and 7·35 (1H, br.s, 6-H).

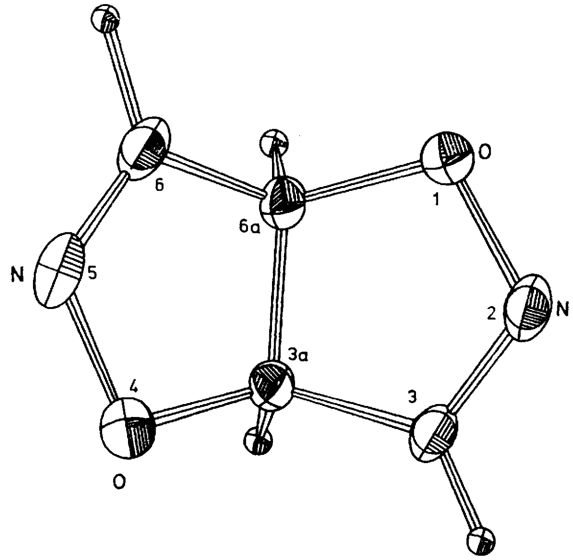

FIGURE. Molecular structure of (**2a**).

These data indicate the presence of an ABX spin system in both (**4a**) and (**5a**), suggesting that a –CH–CH–CH(H′)– unit is present in each structure, and are quite inconsistent with the expected reduction product from (**3**) and its acetate for the eight-membered ring structure.

Thus, the photo-isomer must have the 3a,6a-dihydroisoxazolo[5,4-*d*]isoxazole structure (**2a**) which agrees with its ^{1}H- and ^{13}C-n.m.r. spectra† and the ^{1}H-n.m.r. spectra of its reduction product. Analogous results were obtained when R^1 = Me.‡

In addition, the structure of (**2a**) has been confirmed by single-crystal *X*-ray diffraction. *Crystal data:* $C_4H_4N_2O_2$, colourless needles from Pr^i_2O, space group $P2_1/n$, $a = 8{\cdot}24$, $b = 11{\cdot}17$, $c = 5{\cdot}35$ Å, $\beta = 102{\cdot}75°$, $Z = 4$. Intensity data were collected using Cu-K_α radiation on a Phillips automatic four-circle diffractometer. 565 independent reflections with $I > 3\sigma(I)$ and $\theta < 60°$ were used in the solution. The structure was solved by the direct method,[2] and refined by block diagonal least-squares to a final *R*-index of 0·06.§

As a mechanism for the formation of (**2**), we postulate that fission of the N–N bond of (**1**) by irradiation gives the bis-iminoxyl radical (**6**),[3] followed by ring closure *via* (**7**) to give (**2**). Cyclization of the dinitroso compound (**8**), which has not yet been isolated, is also a possibility.

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† The original assignment of the structure (**3**) was principally based on the ^{1}H- and ^{13}C-n.m.r. spectra as follows: the ^{1}H-n.m.r. spectrum of the photo-isomer of (**1a**) showed two sharp singlets at δ 6·05 (2H) and 7·38 (2H), assigned to two methine protons; its ^{13}C-n.m.r. spectrum showed two signals (δ from Me_4Si) at 88·38 (=CH–) and 143·86 (=CH–). The photo-isomer of (**1b**) showed two signals in the ^{1}H-n.m.r. spectrum at δ 2·10 (6H, s) and 5·75 (2H, s); the ^{13}C-n.m.r. spectrum showed three signals at 10·56 (Me), 89·98 (=CH–), and 153·74 (=CH–).

‡ ^{1}H-n.m.r. data of (**4b**): δ 1·30 (3H, d, *J* 7·0 Hz, 3-Me), 2·08 (3H, s, 6-Me), 3·40 (1H, m, 3-H), 5·07 (1H, dd, *J* 7·0 and 4·0 Hz, 3a-H), and 5·49 (1H, d, *J* 7·0 Hz, 6a-H). ^{1}H-n.m.r. data of (**5b**): δ 1·42 (3H, d, *J* 7·0 Hz, 3-Me), 2·10 (3H, s, N-Ac or 6-Me), 2·12 (3H, s, N-Ac or 6-Me), 4·30 (1H, m, 3-H), 5·21 (1H, dd, *J* 7·0 and 6·0 Hz, 3a-H), and 5·48 (1H, d, *J* 7·0 Hz, 6a-H). The high-resolution mass spectrum of (**2b**) showed that the base peak of *m/e* 82 had been incorrectly assigned to $C_4H_6N_2$ in the previous paper (see ref. 1). The observed mass 82·0285 is assigned to C_4H_4NO (Calc. 82·0291, M^+ – MeCNOH).

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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[2] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

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