X-Ray Crystal Structure of the Chemiluminescent Trioxan 3-Isopropyl-6,6-dimethyl-5-(1-napthylamino)-1,2,4-trioxan

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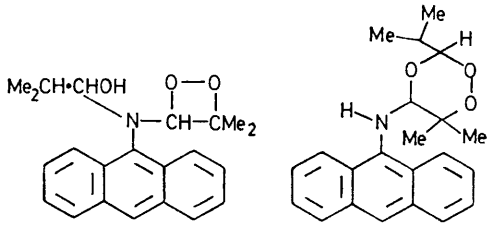
Summary *X*-Ray crystal structure analysis shows that the chemiluminescent compound obtained from 1-naphthylamine and isobutyraldehyde is 3-isopropyl-6,6-dimethyl-5-(1-naphthylamino)-1,2,4-trioxan (**3**); this supports the earlier suggestion that the chemiluminescent compound obtained from 9-anthrylamine and isobutyraldehyde is the trioxan (**2**) rather than the amino-dioxetan (**1**) as previously reported.

RECENTLY we reported that the reaction of 9-anthrylamine and isobutyraldehyde in the presence of atmospheric oxygen gave the amino-dioxetan (**1**).[1] However, in view of the behaviour of a trioxan derived from tetrahydrocarbazole and the known instability of amino-dioxetans, McCapra *et al.*[2,3] proposed that the trioxan structure (**2**) was more likely.

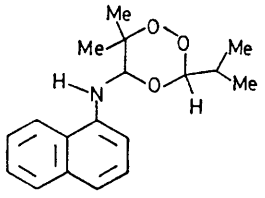
We now report the structure and stereochemistry, determined by *X*-ray crystal structure analysis, of the

chemiluminescent trioxan (**3**), m.p. 79·5—80·0 °C (decomp), derived from 1-naphthylamine and isobutyraldehyde.



(1)

(2)



(3)

Crystal data: $C_{18}H_{23}NO_3$, $M = 301{\cdot}4$, $a = 10{\cdot}061(2)$, $b = 9{\cdot}177(2)$, $c = 18{\cdot}027(2)$ Å, $\beta = 91{\cdot}49°(2)$, $U = 1663{\cdot}8(5)$ Å^3, space group $P2_1/c$, $Z = 4$, $D_m = 1{\cdot}19$ g cm^{-3}, $D_c = 1{\cdot}17$ g cm^{-3}. Intensity data were obtained on a Rigaku automated four-circle diffractometer. The structure was solved by the direct method. All hydrogen atoms were found in the difference map and included in the block-diagonal least-squares refinement. The final R factor was 0·063 for 2920 observed reflections. The molecular structure is shown in the Figure.† This supports the suggestion by McCapra *et al.*[2] that 9-anthrylamine and isobutyraldehyde give a trioxan rather than an amino-dioxetan.

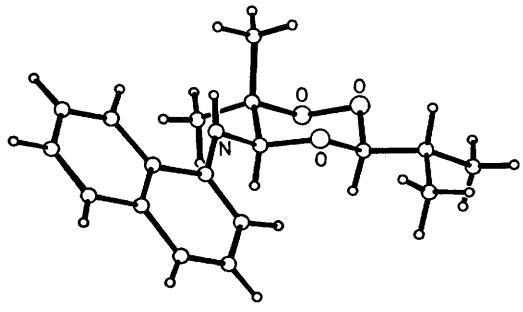


FIGURE. Structure of 3-isopropyl-6,6-dimethyl-5-(1-naphthylamino)-1,2,4-trioxan (**3**).

Similar chemiluminescent trioxans were also obtained from aromatic amines, such as 1-anthrylamine, 1-phenanthrylamine, 3-phenanthrylamine, 9-phenanthrylamine, 9-anthrylamine, and 1-naphthylamine.[4] It is suggested that the stereochemical structure of these trioxans is represented by (**3**) in which the naphthyl group is replaced by an aryl group.

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† 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.

[1] M. Akutagawa, H. Aoyama, Y. Omote, and H. Yamamoto, *J.C.S. Chem. Comm.*, 1976, 180.
[2] F. McCapra, Y. C. Chang, and A. Burford, *J.C.S. Chem. Comm.*, 1976, 608.
[3] T. Goto and H. Nakamura, *Tetrahedron Letters*, in the press.
[4] Unpublished data. Details will be published elsewhere.