

ON THE ISOMERISM OF ARYL-ALKYL-FUROXANS: THE MOLECULAR  
STRUCTURE OF METHYL-P-BROMOPHENYL-FUROXANS

Mariano Calleri, Giovanni Ferraris

III Sezione del Centro Nazionale di Cristallografia del C.N.R.

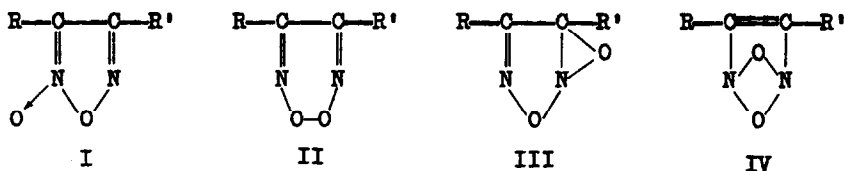
and Davide Viterbo

Istituto di Chimica Fisica dell'Università

Torino, Italia

(Received in UK 8 August 1967)

Continuing a programme of research on the crystal and molecular structure of  $\alpha$ -dioximes and their derivatives, we turned our attention to the oxidation products of aryl-alkyl  $\alpha$ -dioximes with the aim of settling the problem of their molecular configuration. In fact their chemical properties and the existence, in some cases, of isomers with quite different chemical behaviour stimulated a number of hypotheses on their structural formulae. The following configurations were suggested:



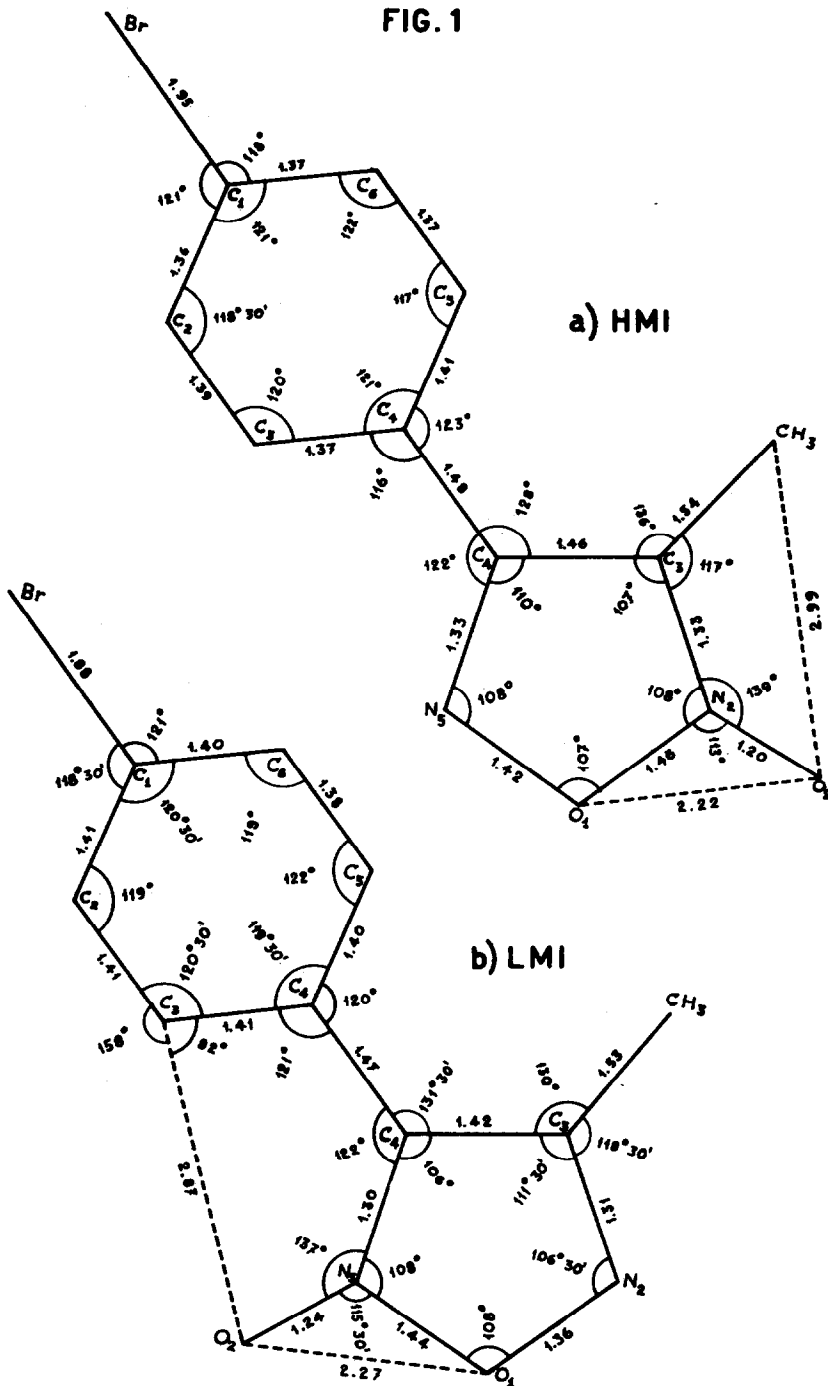
A structural isomerism, based on formulae I and II, was, for instance, supported by several authors (1).

In order to ascertain unequivocally the molecular configuration of one pair of these isomers, we carried out the X-ray crystal-structure analysis of the two compounds, having the empirical formula  $\text{CH}_3-(\text{C}_2\text{N}_2\text{O}_2)-\text{C}_6\text{H}_4\text{Br}$ , obtained from the oxidation of methyl-p-bromophenyl-glyoxime (3). One of the two isomers melts at 88-89°C (LMI), the other at 108-109°C (HMI).

The following crystal data were established:

	$a_0$	$b_0$	$c_0$	$\beta$	$D_m$	Z	Sp.G.
LMI:	12.720Å	10.363Å	7.416Å	97°54'	1.749	4	P2 <sub>1</sub> /n
HMI:	12.648Å	10.136Å	7.499Å	94°52'	1.767	4	P2 <sub>1</sub> /n

FIG. 1



The structures were solved by three-dimensional syntheses of the Patterson and electron density functions. We could thus establish the molecular structure of the two compounds, which appeared to be positional isomers of type I; the values of bond lengths and angles, at the present stage of refinement, are illustrated in FIG. 1a) and 1b). Both molecules are planar and the corresponding atoms have, in the unit cells, very similar values of coordinates except, of course, the extranuclear oxygen atoms of the furoxan residues; the two isomers may therefore be named:

LMI: 5 N-oxide of 3-methyl-4(p-bromophenyl)-1,2,5-oxadiazole

HMI: 2 N-oxide of 3-methyl-4(p-bromophenyl)-1,2,5-oxadiazole.

Such type of isomerism is in accordance with the predictions of Mallory and Cammarata (2) and of Boulton, Katritzky and Majid Hamid (personal communication) based on n.m.r. spectra and on thermal interconvertibility of the isomers.

We postpone the discussion on bonds and on the noteworthy features of these isomers to the completion of the study of their crystal and molecular structure, which will be published elsewhere.

Aknowledgements. We are greatly indebted to prof. E. Borello for suggesting this work and to Drs. A.J. Boulton and J.C. Speakman for their advices.

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