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Photochemical Studies

XI. The Photolysis of Quinoxaline *N*-Oxides to Benz[d][1,3,6]-oxadiazepines. An X-Ray Study *,**

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The structure of the main product in the photolysis of 2,3-bis(4-bromophenyl)quinoxaline *N*-oxide (Id) is shown to be 2,4-bis(4-bromophenyl)benz[d][1,3,6]oxadiazepine ** (IId) by X-ray crystallography. By comparing the infrared and ultraviolet spectra of IId with those of the previously obtained photoproducts (IIa—c)[1,3-4] from quinoxaline *N*-oxides (Ia—c), it is found that IIa—c also must have the benz[d][1,3,6]oxadiazepine ** structure. This is in agreement with their reported hydrolysis products.[3-4]

In continuation of recent work describing the formation of seven-membered rings in the photolysis of heteroaromatic *N*-oxides[1,5-7] we have examined the main photolysis product (IId) of 2,3-bis(4-bromophenyl)quinoxaline *N*-oxide (Id) by X-ray crystallography.

The electron density projection, $\varrho(xz)$, of IId (Fig. 1) shows the molecule well resolved. The bonds in the seven-membered ring seem to be roughly

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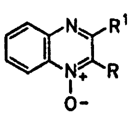
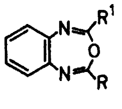
* For paper X in this series, see Ref. 1.

** In this series benzoxazepines, benzoxadiazepines, *etc.* are given IUPAC[2] "fusion names", the last bracket being inserted to avoid confusion of the numbering of the hetero-atoms in the uncondensed seven-membered ring with the numbering of the final ring system (this bracket has not been used in the preceding papers).[1,5-7] In *Chemical Abstracts* benzoxadiazepine, *etc.* are treated as semitrivial names: *e.g.* 2,4-bis(4-bromophenyl)-3,1,5-benzoxadiazepine. (In paper X of this series[1] a misprint is found: Instead of -benz[d][1,3,5]- read -benz[d][1,3,6]-). Both nomenclatures lead to the same numbering of the final ring system.



I



II

a: $R = C_6H_5$; $R^1 = H$
b: $R = H$; $R^1 = C_6H_5$
c: $R = R^1 = C_6H_5$
d: $R = R^1 = p\text{-}Br\text{-}C_6H_4$

parallel to the plane of projection. The projections of the distances between the atoms in the seven-membered ring show that the only possible bonds between the atoms are those shown in the figure. The heights of the peaks corresponding to N(1) and N(5) (Fig. 1) are on an arbitrary scale 126 and 155, respectively, whereas the heights of most of the peaks corresponding to carbon atoms are between 110 and 130 with a few extreme exceptions (84 and 151 for peaks corresponding to carbon atoms in benzene rings). The height of the peak O(3) is 183. By considering this, we conclude that the only possible structure is the one shown, (IId); *cf.* Fig. 1.

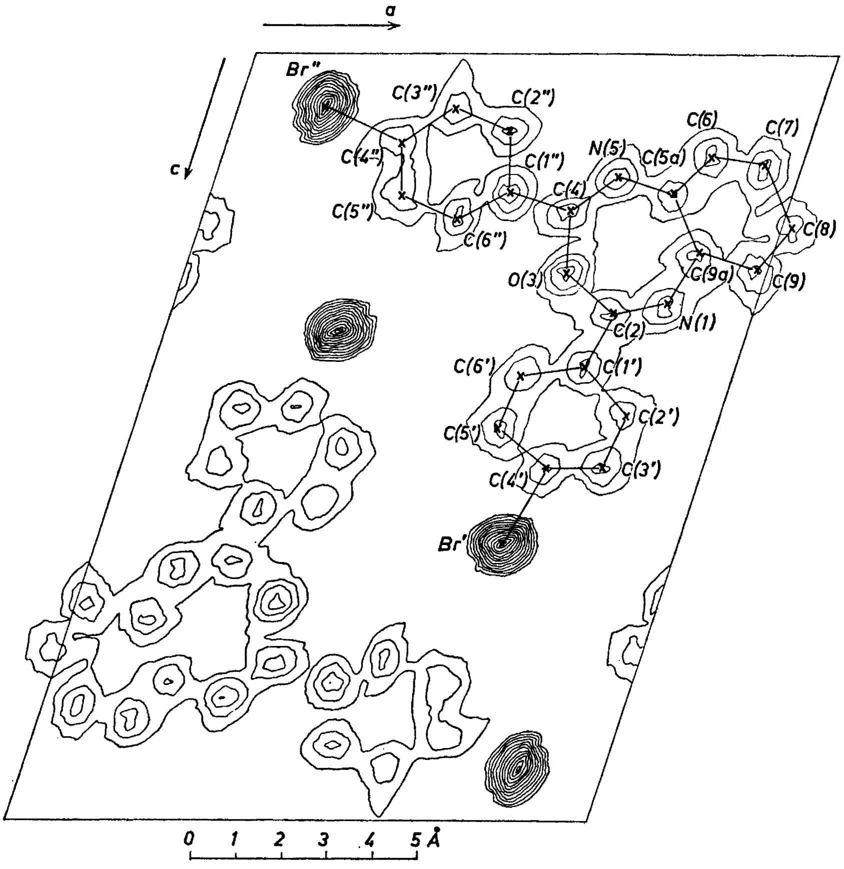
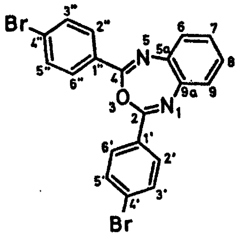
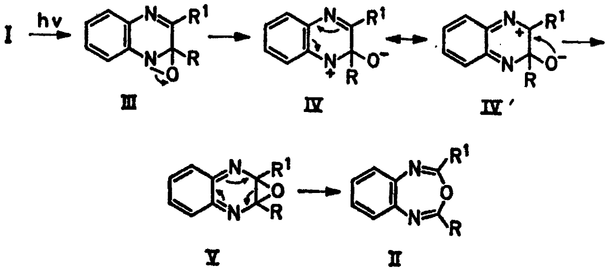


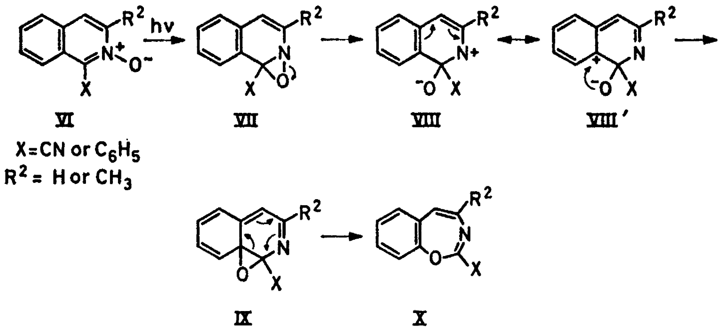
Fig. 1. The electron density projection $\varrho(xz)$ of IId drawn in an arbitrary scale.



II d

By comparing the infrared absorption in the 1600 cm^{-1} region and the long wavelength ultraviolet spectra of IIa—d (Table 1) there seems to be no doubt that they all have the structures shown. The previously described hydrolysis experiments[3-4] are in excellent agreement with this assignment.





X = CN or C_6H_5
R^2 = H or CH_3

DISCUSSION

The photoinduced formation of seven-membered rings in the quinoline *N*-oxide series[5-6] is believed to occur *via* oxaziridines. The further reactions of the oxaziridines are at present thought to occur by heterolysis — photoinduced or thermal — resulting in a zwitterionic species as common intermediate for both carbostyril[8] and oxazepine formation,[6] the latter possibly by way of an oxirane intermediate.[4] Similar reaction sequences can be depicted

Table 1. Infrared absorption in the 1600-cm^{-1} region and long wavelength ultraviolet absorption of benz[d][1,3,6]oxadiazepines.

	IR		UV		
Compound	cm^{-1}	Recorded in	λ_{max}, mμ	log ε	Recorded in
IIa—IIb [4]	1675	CCl_4	320	3.84	$ClCH_2CH_2Cl$
IIc	1670	KBr	325 sh	3.89	96 % EtOH
IId	1670	KBr	332 sh	3.53	96 % EtOH

for the formation of seven-membered rings in the photolysis of the isoquinoline [7] and the present series,[1,4] as shown below. However, it should be emphasized that these schemes are purely speculative. The formation of the seven-membered rings (II and X) *via* the zwitterionic species (IV—IV′ and VIII—VIII′) is here shown with the valence tautomers (V and IX) as intermediates. However, the formation of the seven-membered rings may as well occur directly from the zwitterions.[6]

There is at present no evidence to suggest an equilibrium between V and II or IX and X, respectively. However, the formation of 3-hydroxyquinolines from a series of 2-cyanobenz[d][1,3]oxazepines described by Kaneko *et al.*[9] indicates that there may be such an equilibrium in the latter compounds.*

EXPERIMENTAL

The microanalyses and the spectroscopy were carried out as previously described.[6,8]

X-Ray crystallography. IId crystallized from a benzene-carbon tetrachloride solution as hair-thin triclinic crystals. The cell dimensions, determined from a rotation photograph (rotation around the *b*-axis), and from *h*0*l*, *h*1*l* and *h*2*l* Weissenberg photographs, using the graphical method of Hulme,[12] are: $a = 12.8$ Å, $b = 4.09$ Å, $c = 17._7$ Å, $\alpha = 87._7°$, $\beta = 108._1°$, $\gamma = 98._4°$, $z = 2$. The structure determination shows the space group to be $P\bar{1}$.

A crystal of dimensions 0.02 × 0.03 × 1.0 mm^3 was rotated around the needle axis, and Weissenberg photographs of the *h*0*l* reflections were made, using Cu$K\alpha$ radiation and multiple film technique. The intensities were estimated visually. No correction for absorption was applied.

The Patterson function $P(xz)$ was calculated from 303 independent *h*0*l* reflections, and using the assumption that the space group is $P\bar{1}$, the structure was solved by heavy atom techniques. By three cycles of full matrix least squares refinements [13] of the coordinates and the individual isotropic temperature factors, the conventional *R*-index was lowered to 11.7 %. The final parameters are given in Table 2, together with their estimated standard deviations.

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* For a very recent discussion of similar valence tautomerisms see Refs. 10—11.

Table 2. Final positional and thermal parameters and their estimated standard deviations.

Atom	x/a	$\sigma(x/a)$	z/c	$\sigma(z/c)$	B (Å^2)	σB (Å^2)
Br′	0.7017	0.0005	0.6400	0.0003	4.70	0.17
Br″	0.1489	0.0005	0.0689	0.0003	4.46	0.17
N(1)	0.849	0.003	0.326	0.002	4.5	1.1
C(2)	0.757	0.003	0.338	0.002	2.8	1.1
O(3)	0.656	0.002	0.288	0.002	2.7	0.7
C(4)	0.629	0.004	0.205	0.003	3.1	1.2
N(5)	0.689	0.003	0.159	0.002	3.2	1.1
C(5a)	0.797	0.003	0.186	0.002	2.3	1.0
C(6)	0.838	0.004	0.129	0.003	2.6	1.1
C(7)	0.937	0.004	0.143	0.003	3.0	1.4
C(8)	1.018	0.006	0.224	0.004	9.3	2.5
C(9)	0.982	0.003	0.280	0.003	3.1	1.1
C(9a)	0.872	0.004	0.261	0.003	3.4	1.2
C(1′)	0.739	0.004	0.409	0.003	2.7	1.1
C(2′)	0.840	0.004	0.469	0.003	3.2	1.4
C(3′)	0.833	0.003	0.541	0.002	2.8	1.0
C(4′)	0.726	0.004	0.544	0.003	3.9	1.3
C(5′)	0.624	0.003	0.484	0.002	1.5	1.0
C(6′)	0.636	0.003	0.418	0.003	2.8	1.2
C(1″)	0.517	0.004	0.178	0.003	2.7	1.2
C(2″)	0.479	0.003	0.104	0.002	2.2	1.0
C(3″)	0.373	0.003	0.070	0.003	2.7	1.1
C(4″)	0.299	0.005	0.116	0.004	5.4	1.7
C(5″)	0.329	0.004	0.187	0.003	3.2	1.2
C(6″)	0.439	0.003	0.217	0.002	0.5	0.8

2,3-Bis(4-bromophenyl)quinoxaline. This compound was prepared in 80 % yield by the method described for 2,3-diphenylquinoxaline.[14] M.p. 188–190°. (Found: C 54.50; H 2.90; N 6.26; Br 36.49. Calc. for $C_{20}H_{12}Br_2N_2$: C 54.60; H 2.75; N 6.36; Br 36.30).

2,3-Bis(4-bromophenyl)quinoxaline N*-oxide (Id).* This compound was prepared by oxidation of 2,3-bis(4-bromophenyl)quinoxaline with 3-chloroperbenzoic acid according to the method previously described.[6] Time of oxidation: 65 h. Yield 65 %. M.p. 216–219°. (Found: C 52.55; H 2.77; N 5.94; Br 34.70. Calc. for $C_{20}H_{12}Br_2N_2O$: C 52.71; H 2.65; N 6.14; Br 35.04).

2,4-Bis(4-bromophenyl)benz[d][1,3,6]oxadiazepine (IId). By following the previously described irradiation procedure,[8] method B, with acetone as solvent, IId was obtained in 70 % yield. M.p. 194–196°. (Found: C 52.50; H 2.74; N 5.97; Br 35.04. Calc. for $C_{20}H_{12}Br_2N_2O$: C 52.71; H 2.65; N 6.14; Br 35.04).

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