

The Structure of *N*-[3-Phenyl-5-(1,2,3,4-oxatriazolio)]-phenylamide at 105 K

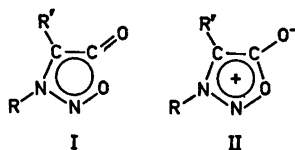
T. OTTERSEN,^a C. CHRISTOPHERSEN^b and S. TREPPENDAHL^c

^a Department of Pharmacy, University of Oslo, Oslo 3, Norway, ^b Department of General and Organic Chemistry, University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark and ^c Institute for Chemistry, Faculty of Medicine, University of Copenhagen, Rådmandsgade 71, DK-2200 Copenhagen, Denmark

The crystal and molecular structure of the *meso*-ionic title compound, C₁₃H₁₀N₄O, have been determined by X-ray methods using 2667 reflections above background level collected by counter methods at 105 K. The crystals are monoclinic, space group *P*2₁/*c*, with cell dimensions: *a* = 5.233(2) Å; *b* = 18.846(6) Å; *c* = 11.643(2) Å, β = 105.71°(2), with 4 molecules per unit cell. The structure model was refined to an *R*-factor of 0.047. In order to reduce the influence of the valence electrons all reflections with $\sin \theta/\lambda < 0.5 \text{ \AA}^{-1}$ were excluded in the last stages of the refinement procedure (leaving 1658 *F*_o's, *R* = 0.058). The central five-membered ring is found to be planar and the bond lengths within this ring indicate a resonance stabilized system, as has been found for sydrones. The planes of the two benzene rings are tilted 11.7 and 8.0°, respectively, with respect to the plane of the central oxatriazolio-ring.

meso-Ionic structures have recently attracted considerable interest because of their marked pharmacological activity associated with certain members of this group of organic compounds.¹ Among these compounds *O*-3-alkyl-5-(1,2,3,4-oxatriazolio)oxides have been shown to exhibit a marked hypotensive effect.² Molecular orbital calculations have been performed on the latter systems and a successful correlation between the predicted charge densities in these compounds and the isoelectronic sydrones, and their hypotensive potency has been obtained.³

Several structure investigations of sydrones have been reported.^{3,4} These five-membered rings are found to be planar with bond lengths indicating a conjugated system, except for the relatively long intraring CO distance (1.40—1.42



Å). Hope and Thiessen⁴ have therefore proposed I as the best single formula representation of a sydrone. This structure is in agreement with experimental evidence that the sydrone ring is aromatic and emphasize that the exocyclic C—O bond is of normal double bond length, whereas representation II⁵ reflects the low bond order found for this bond by molecular orbital calculations using a normal σ -skeleton (see Ref. 2 and references therein).

The related 3-substituted *N*-[5-(1,2,3,4-oxatriazolio)]amides have attracted less interest, undoubtedly because until recently only one example of this class of compounds was recorded under this formula in the literature. However, it has been shown that a compound isolated by Busch and Becker⁶ in 1896 and analogous compounds isolated by Busch and Schmidt⁷ in 1929 first described as "isotetrazolon" and later as "azo-1,3-endoxy-hydrazomethylen" are 3-substituted *N*-[5-(1,2,3,4-oxatriazolio)]amides.⁸ As a synthetic method for these compounds is now available⁹ a systematic investigation of the structural, pharmacological, and physico-chemical properties of these compounds may be carried out.

In order to establish the constitution rigorously and to investigate the geometry of this

meso-ionic system a crystal structure investigation was undertaken. It is of interest to see if this five-membered ring system has the same structural properties as the sydnones and to get evidence about the "best" structural formula representation. These structural parameters may be helpful in the investigations of other properties of this class of compounds.

EXPERIMENTAL

The title compound⁸ was recrystallized by very slow cooling of a saturated (at boiling point) solution in benzene:cyclo-hexane 1:2 to -20°C .

Oscillation, Weissenberg and precession photographs indicated monoclinic symmetry; all reflections ($h0l$) for l odd and ($0k0$) for k odd, were systematically absent. This uniquely defines the space group as $P2_1/c$.

A computer-controlled Syntex-P1 four-circle diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation and equipped with an Enraf-Nonius liquid nitrogen cooling device (modified by H. Hope) was utilized for preliminary experiments and for the measurement of diffraction intensities. The work was carried out using a crystal of dimensions $0.53 \times 0.18 \times 0.10$ mm. Unit cell parameters were determined by a least-squares treatment of the angular coordinates of fifteen symmetry-independent reflections with 2θ -values from 30 to 40° . The temperature at crystal site was 105 K .

Three-dimensional intensity data were recorded using the $\omega-2\theta$ scanning mode with scan speed variable from 2 to $12^{\circ}\text{min}^{-1}$, depending on the peak intensity of the reflections. Background counting time was equal to $0.7 \times$ scan time. Reflections with 2θ -values larger than 50° which had integrated counts of less than 8 cps, determined in a 2 s scan over the reflection, were not measured. The variations in the intensities of three standard reflections which were remeasured after every hundred reflections were random and less than three times their standard deviations. Accordingly no corrections were applied for these variations.

The estimated standard deviations were taken as the square root of the total counts with a 2% addition for experimental uncertainties. Of the 3196 symmetry-independent reflections measured ($2\theta_{\text{max}}=80^{\circ}$), 2667 had intensities larger than twice their standard deviations. These were regarded as "observed" reflections, and the remaining reflections were excluded from further calculations. The intensities were corrected for Lorentz and polarization effects. The computer program used, as well as programs subsequently employed, is part of a local assembly of computer programs for CYBER-74 and is described in Ref. 10.

The atomic scattering factors used were those of Doyle and Turner¹¹ for carbon, oxygen and nitrogen, and of Stewart *et al.*¹² for hydrogen.

CRYSTAL DATA

N-[3-Phenyl-5-(1,2,3,4-oxatriazolio)]phenylamide, $\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}$, monoclinic. Cell dimensions at 105 K :

$a=5.233(002)\text{ \AA}$; $b=18.846(006)\text{ \AA}$;

$c=11.643(002)\text{ \AA}$; $\beta=105.71(02)^{\circ}$.

Figures in parentheses are estimated standard deviations.

$V=1105.2\text{ \AA}^3$, $M=238.2\text{ amu}$; $Z=4$;

$D_{\text{calc}}=1.431\text{ g/cm}^3$; $F(000)=496$.

Absent reflections: ($h0l$) for l odd; ($0k0$) for k odd; space group $P2_1/c$.

STRUCTURE DETERMINATION AND REFINEMENTS

The phase problem was solved by a computer procedure¹³ based on direct methods utilizing tangent refinement.

The structure model was refined to a conventional R of 0.11 . At this point the hydrogen

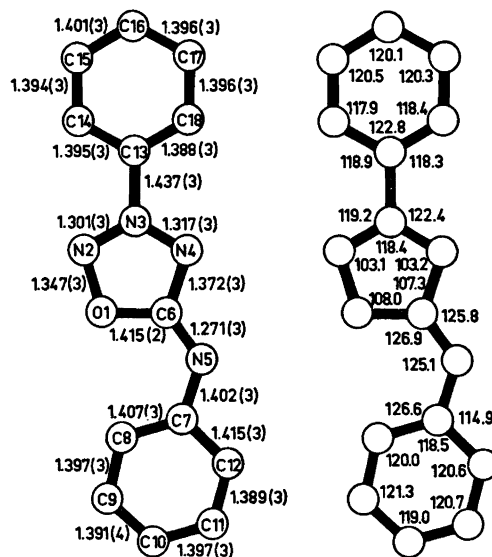


Fig. 1. Bond lengths (\AA) with estimated standard deviations ($\text{\AA} \times 10^3$ in parentheses), and bond angles ($^{\circ}$). E.s.d.'s in bond angles are 0.2° . Structure model obtained using high-angle data only in the refinement.

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations ($\times 10^4$) for non-hydrogen atoms. The temperature factor is given by $\exp - (B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$. Results from the refinement using high-angle data only.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O1	33817(41)	94083(10)	88797(16)	1821(58)	128(4)	196(10)	236(25)	257(37)	3(10)
N2	13470(38)	98861(10)	87737(14)	1935(61)	126(4)	218(9)	183(24)	274(37)	-16(10)
N3	3033(45)	99225(11)	76263(16)	1659(64)	89(5)	180(10)	15(28)	299(38)	-11(11)
N4	13630(37)	95395(10)	69274(14)	1649(55)	108(4)	203(9)	183(25)	282(34)	2(9)
N5	50464(43)	87727(11)	74440(16)	1829(61)	120(4)	216(10)	287(27)	387(38)	42(10)
C6	34146(46)	91961(12)	77179(18)	1619(66)	103(4)	210(10)	103(27)	269(40)	32(11)
C7	71146(41)	84188(11)	82632(17)	1436(62)	92(4)	250(11)	32(26)	395(41)	42(11)
C8	76142(47)	84185(13)	95127(19)	1629(68)	137(5)	256(11)	104(31)	266(43)	36(13)
C9	97660(50)	80378(13)	102138(19)	1821(69)	117(5)	277(12)	-57(31)	66(46)	39(12)
C10	114545(48)	76578(13)	97022(22)	1578(67)	109(5)	363(14)	-15(30)	-104(48)	20(13)
C11	109822(49)	76615(13)	84626(21)	1690(68)	113(5)	374(14)	120(30)	242(49)	-5(13)
C12	88418(46)	80319(13)	77474(19)	1654(70)	109(5)	303(12)	117(30)	318(46)	0(12)
C13	-19048(41)	103906(11)	71654(17)	1339(59)	81(4)	216(10)	-17(24)	252(38)	-7(10)
C14	-32013(46)	106844(12)	79533(18)	1576(64)	106(5)	252(11)	75(28)	466(42)	-18(11)
C15	-53141(47)	111445(12)	74898(21)	1598(69)	115(5)	343(13)	146(29)	502(48)	-10(13)
C16	-61185(47)	112943(13)	62662(21)	1531(67)	106(5)	342(13)	130(29)	313(46)	13(12)
C17	-47805(48)	109906(13)	55017(19)	1726(70)	110(5)	267(11)	142(29)	163(44)	18(12)
C18	-26419(44)	105344(12)	59506(17)	1571(64)	103(5)	218(11)	35(27)	312(41)	0(11)

Table 2. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters with estimated standard deviations for hydrogen atoms. Results from the refinement using all observed data.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H19	643(4)	868(1)	987(2)	2.6(5)
H20	1012(4)	805(1)	1105(2)	2.4(4)
H21	1292(4)	741(1)	1018(2)	2.1(4)
H22	1218(4)	742(1)	810(2)	2.1(4)
H23	843(4)	802(1)	690(2)	2.7(5)
H24	-254(4)	1058(1)	877(2)	2.3(4)
H25	-614(4)	1136(1)	799(2)	2.4(4)
H26	-762(4)	1160(1)	598(2)	1.9(4)
H27	-533(4)	1109(1)	467(2)	2.5(4)
H28	-163(4)	1033(1)	544(2)	2.3(4)

atoms were placed in calculated positions and anisotropic thermal parameters for all non-hydrogen atoms were introduced. Full-matrix least-squares refinement of all positional parameters, anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms using all observed reflections converged to a weighted R_w of 0.047 and a conventional R of 0.054.

Earlier structure determinations¹⁴⁻¹⁶ have indicated that structural parameters found for molecular systems like the present one are significantly influenced by the asphericity of the valence electron densities. By a systematic variation of the lower $\sin \theta/\lambda$ cutoff for reflections used in the refinement, it was found that this asphericity had little or no effect when all reflections with $\sin \theta/\lambda < 0.5$ were excluded from the refinements. This is in agreement with earlier results.^{16,17} Least-squares refinement of all parameters (*s*) involving non-hydrogen atoms using the 1658 observed reflections (*m*) with $\sin \theta/\lambda > 0.5$ resulted in a conventional R of 0.058, an R_w of 0.055, and an R -factor for the total data set of 0.063. The "goodness of fit" ($\{(\sum w(F_o - |F_c|)^2)/(m-s)\}^{1/2}$) is 1.20. Atomic parameters for non-hydrogen atoms, obtained in this refinement are listed in Table 1, and parameters for hydrogen atoms, from the refinement using all observed reflections, are given in Table 2. A listing of observed and calculated structure factors is available from the authors upon request.*

* Also available from Department of Chemistry, University of Oslo, Oslo 3, Norway.

Standard deviations in molecular parameters were calculated from the correlation matrix ignoring standard deviations in cell parameters.

The r.m.s. difference between the observed U_{ij} 's and those calculated from the "rigid body" model²⁴ is 0.0014 Å². However, the corrections in atomic positional parameter for the librational motion are extremely small, giving maximum corrections in bond lengths of 0.001 Å; these corrections are, therefore, not included.

Table 3. Deviations (Å $\times 10^3$) from least-squares planes through the three ring systems. The deviations for those atoms used to define the plane are given in italicized figures.

Atom	Deviations (Å $\times 10^3$)		
	Plane A	Plane B	Plane C
O1	<i>5</i>	-291	
N2	<i>-5</i>		-262
N3	<i>2</i>		-9
N4	<i>2</i>	-103	197
N5	<i>-34</i>	-1	
C6	<i>-6</i>	-115	
C7	<i>-25</i>	<i>2</i>	
C8		<i>-3</i>	
C9		<i>1</i>	
C10		<i>3</i>	
C11		<i>-4</i>	
C12		<i>2</i>	
C13	-28		<i>1</i>
C14			<i>4</i>
C15			<i>-6</i>
C16			<i>3</i>
C17			<i>2</i>
C18			<i>-3</i>

Angle between plane A and plane B: 8.0°
Angle between plane A and plane C: 11.7°

Table 4. Selected dihedral angles (°) with estimated standard deviations. The angles are positive in a right-hand screw.

Dihedral angle	(°)
C7-N5-C6-O1	1.6(4)
C7-N5-C6-N4	-179.2(2)
C6-N5-C7-C8	5.8(4)
C6-N5-C7-C12	-173.8(2)
N4-N3-C13-C18	-11.3(3)
N2-N3-C13-C14	-12.6(3)

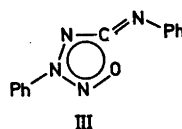
DISCUSSION

Bond lengths and bond angles are given in Fig. 1, where the numbering of the atoms is indicated. Deviations from least-squares planes through the three rings are listed in Table 3 and some selected dihedral angles in Table 4.

The central oxatriazolium ring is planar while the two atoms (N5 and C7) bonded to this ring deviate significantly from the least-squares plane through the five ring atoms. The planes of the two phenyl groups are twisted only 8.0° (C7—C12) and 11.7° (C13—C18) with respect to the central ring. However, the two bonds C7—N5 and C13—N3 which connect the two phenyl groups with the central *meso*-ionic system are relatively long (1.402 Å and 1.437 Å, respectively) and may indicate that there is only a small, if any, coupling between the conjugation in the two phenyl rings and in the central ring system. Furthermore there is the "pure" C6—N5 double bond.

The N—N, N—C, and N—O bonds in the central ring indicate a conjugated system. They may be compared with the N—N bond in pyridazine (1.330 Å)¹⁸ and *s*-tetrazine (1.321 Å),¹⁹ the C—N bonds in a series of 3,6-pyridazinediones^{14–16,20} (1.345–1.374 Å), and the N—O bond in 1,2,5-oxadiazole (1.380 Å).²¹ However, the C—O bond of 1.415 Å is very much longer than that in furan²² (1.36 Å), while the exocyclic C=N distance (1.271 Å) is close to the pure C—N double bond of 1.278 Å.²³ A similar situation is found for the sydnones^{3,4} and in these compounds are the exocyclic $\angle C-C-O$ opened to about $135-137^\circ$. An opening of the corresponding $\angle N4-C6-N5$ is not found in the present oxatriazolium-amide. The $\angle O1-C6-N5$ and the $\angle N4-C6-N5$ are almost equal (126.9 and 125.8° , respectively). Further, the angles in the central ring deviate significantly from the corresponding angles in the sydnones,^{3,4} e.g. the angle at O1 is 108° while it is 111° in the latter structures.

Although the angles around C6 are not distorted in the same manner as in sydnones, the long O1—C6 distance and the pure N5=C6 double bond imply an electronic structure close to that of the sydnones. The "best" single formula representation of the oxatriazoliumamide system is probably III in agreement to that proposed for sydnones⁴ (I). This representation



is only meant to emphasize that the C=N bond is of normal double bond length. A formula representation similar to II will be in sharp contradiction to this observation.

As was pointed out by Hope and Thiessen,⁴ a literal interpretation of this formula (III) will give a net positive charge of 0.8 e on N3 and an equal negative charge distributed over the other ring atoms.

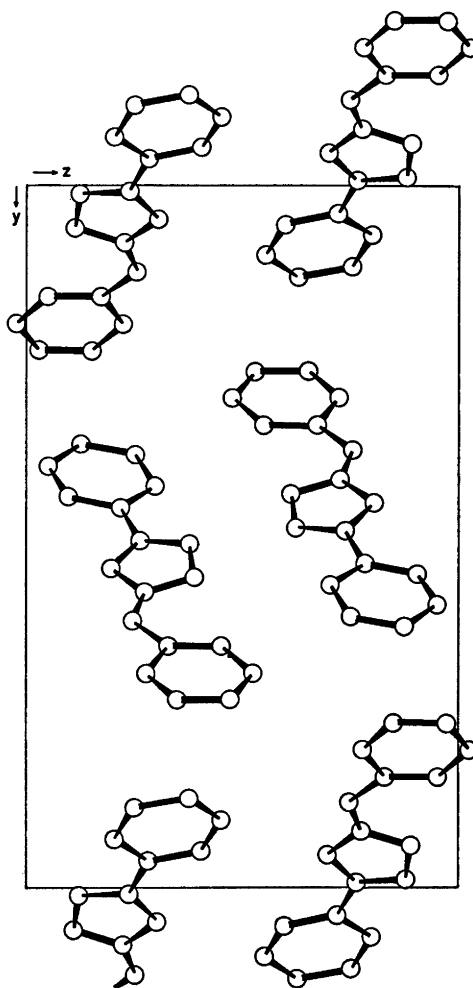


Fig. 2. The crystal structure as seen along the *a*-axis.

The C7—C12 phenyl ring has a mean bond length of 1.399 Å with an r.m.s. deviation of 0.009 Å. The two bonds C7—C8 and C7—C12 are slightly longer than this (1.407 and 1.415 Å, respectively) and may indicate a distortion around C7 caused by the amide group. The opening of $\angle N5-C7-C8$ to 126.6° is probably caused by repulsion between the hydrogen bonded to C8 (H19) and O1. The other phenyl ring is normal, mean bond length 1.395 Å with an r.m.s. deviation of 0.004 Å.

A view of the molecular packing in the crystal is given in Fig. 2. The packing is dominated by van der Waals forces with many short intermolecular contacts.

REFERENCES

1. Thomas, T. L., Fedorchuk, M., Shetty, B. V. and Anderson, F. E. *J. Med. Chem.* 13 (1970) 196.
2. Kier, L. B., Al-Shamma, A., Hahn, R. and Tye, A. *J. Pharm. Sci.* 55 (1966) 1467.
3. Bärnighausen, H., Jellinek, F., Munnik, J., and Vos, A. *Acta Crystallogr.* 16 (1962) 471.
4. Hope, H. and Thiessen, W. *Acta Crystallogr. B* 25 (1969) 1237.
5. Baker, W., Ollis, W. D. and Poole, V. D. *J. Chem. Soc.* (1949) 307.
6. Busch, M. and Baker, J. *Ber. Deut. Chem. Ges.* 29 (1896) 1686.
7. Busch, M. and Schmidt, W. *Ber. Deut. Chem. Ges.* 62 (1929) 1449.
8. Christophersen, C. and Treppendahl, S. *Acta Chem. Scand.* 25 (1971) 625.
9. Christophersen, C. and Treppendahl, S. *Acta Chem. Scand.* 26 (1972) 858.
10. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
11. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A* 24 (1968) 390.
12. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
13. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
14. Ottersen, T. *Acta Chem. Scand.* 27 (1973) 797.
15. Ottersen, T. *Acta Chem. Scand. A* 28 (1974) 661.
16. Ottersen, T. *Acta Chem. Scand. A* 28 (1974) 666.
17. Ottersen, T. *Acta Chem. Scand. A* 28 (1974) 1145.
18. Werner, W., Dreizler, D. and Rudolph, H. *O. Z. Naturforsch.* 22a (1967) 531.
19. Bertinotti, F., Giacomello, G. and Liquori, A. M. *Acta Crystallogr.* 9 (1956) 510.
20. Ottersen, T. *Acta Chem. Scand.* 27 (1973) 835.
21. Saegbarth, E. and Cox, A. P. *J. Chem. Phys.* 43 (1965) 166.
22. Bak, B., Christensen, D., Dixon, W. B., Hansen-Nygaard, L., Rastrup-Andersen, J. and Schoffländer, M. *J. Mol. Spectrosc.* 9 (1962) 124.
23. Fischers-Hjalmars, I. and Sundbom, M. *Acta Chem. Scand.* 22 (1968) 2237.
24. Shoemaker, V. and Trueblood, K. N. *Acta Crystallogr. B* 24 (1968) 63.

Received July 29, 1974.