2-Phenyl-4-*p*-tolylbenz[*f*]-1,3,5-oxadiazepine

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Abstract. $C_{21}H_{15}ON_2$, $M = 311 \cdot 4$. Orthorhombic, $a = 19 \cdot 589$ (2), $b = 8 \cdot 442$ (1), $c = 19 \cdot 692$ (2) Å, $U = 3256 \cdot 6$ Å^3, $D_m = 1 \cdot 26$ (by flotation), $Z = 8$, $D_c = 1 \cdot 27$ g cm^{-3}, $F(000) = 1312$, space group *Pbca* (from systematic absences). Mo $K\alpha$ radiation, $\lambda = 0 \cdot 7107$ Å, μ(Mo K) $= 0 \cdot 86$ cm^{-1}. The analysis confirms that the title compound contains the unusual 1,3,5-oxadiazepine ring system, which adopts a boat conformation, and in which the two C=N double bonds are apparently localized.

Introduction. A small crystal was exposed to Zr-filtered Mo radiation on a Hilger & Watts Y290 diffractometer, and the intensities of 1304 independent reflexions $[I \geq 2\sigma_I, \sigma_I = \sqrt{(I + B_1 + B_2)}]$ were measured by the θ, ω-scan technique in the range $2\theta = 0$–$50°$. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was resolved by the symbolic addition approach, an initial E map based on 237 reflexions ($|E| \geq 1 \cdot 25$) revealing all non-hydrogen atoms. Refinement of positional and thermal parameters by least squares converged when R was $0 \cdot 056$. A difference synthesis calculated after the initial cycles of refinement revealed all the H atoms, which were included but not refined in subsequent cycles. The data were weighted according to $w = A/|F_o|^2$, the final value of A being $18 \cdot 0$.

Final fractional coordinates and thermal parameters

Table 1. *Atomic coordinates and thermal parameters*

(*a*) Fractional coordinates ($\times 10^4$) (hydrogen $\times 10^3$)

	x	y	z
O(1)	3137 (1)	1529 (4)	5119 (1)
C(2)	3086 (2)	2158 (6)	4465 (2)
N(3)	3606 (1)	2489 (5)	4110 (2)
C(4)	4267 (2)	2320 (6)	4386 (2)
N(5)	4468 (1)	2830 (5)	4970 (2)
C(6)	4229 (2)	4524 (5)	5924 (2)
C(7)	3807 (2)	5055 (7)	6438 (2)
C(8)	3157 (2)	4412 (7)	6510 (2)
C(9)	2926 (2)	3274 (7)	6067 (2)
C(10)	3352 (2)	2743 (6)	5555 (2)
C(11)	4009 (2)	3371 (6)	5464 (2)
C(21)	2378 (2)	2392 (6)	4225 (2)
C(22)	2259 (2)	3302 (7)	3647 (2)
C(23)	1594 (2)	3572 (8)	3435 (2)
C(24)	1053 (2)	2906 (7)	3786 (2)
C(25)	1166 (2)	2094 (7)	4352 (2)
C(26)	1831 (2)	1735 (6)	4577 (2)
C(41)	4783 (2)	1700 (6)	3913 (2)
C(42)	5406 (2)	1137 (6)	4165 (2)

Table 1 (*cont.*)

C(43)	5902 (2)	574 (6)	3734 (2)
C(44)	5798 (2)	521 (6)	3033 (2)
C(45)	5175 (2)	1026 (7)	2783 (2)
C(46)	4674 (2)	1620 (7)	3216 (2)
C(441)	6356 (2)	−91 (8)	2575 (2)
H(6)	469	506	590
H(7)	398	588	677
H(8)	286	489	689
H(9)	245	?94	614
H(22)	270	401	344
H(23)	149	475	313
H(24)	55	330	360
H(25)	79	126	460
H(26)	196	98	494
H(42)	543	72	465
H(43)	637	24	401
H(45)	509	91	228
H(46)	423	185	302
H(441)	627	0	217
H(442)	660	−124	279
H(443)	672	103	252

(*b*) Anisotropic temperature factors (Å$^2 \times 10^4$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	448	624	576	−76	−45	175
C(2)	406	602	476	−15	−30	72
N(3)	315	712	531	13	−19	72
C(4)	340	587	551	3	−32	56
N(5)	357	591	626	35	9	6
C(6)	511	716	601	4	−17	−14
C(7)	644	680	667	69	−2	−44
C(8)	641	845	607	99	84	49
C(9)	448	860	578	−4	60	101
C(10)	436	534	528	22	−38	111
C(11)	371	605	540	37	−20	85
C(21)	338	553	500	22	−19	−6
C(22)	427	844	549	29	−23	83
C(23)	501	1051	673	64	−96	111
C(24)	417	851	717	44	−86	−107
C(25)	398	767	712	−82	19	−75
C(26)	411	671	616	−72	4	26
C(41)	359	626	540	−8	−4	35
C(42)	447	651	542	87	−64	38
C(43)	449	572	651	64	−16	−13
C(44)	457	537	608	15	19	−29
C(45)	501	834	529	37	−26	22
C(46)	370	866	564	56	−55	56
C(441)	619	1006	679	153	79	−142

Mean estimated standard deviations (Å$^2 \times 10^4$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	20	25	21	20	21	24
N	22	26	24	19	27	25
C	26	31	29	26	27	28

Table 2. *Interatomic distances* (Å) *and angles* (°)
for the benzoxadiazepine ring system

(*a*) Bonded distances (Å)

O(1)–C(2)	1·396 (5)	C(6)—C(7)	1·381 (6)
O(1)–C(10)	1·403 (5)	C(6)—C(11)	1·397 (6)
C(2)–N(3)	1·268 (5)	C(7)—C(8)	1·391 (7)
N(3)–C(4)	1·412 (4)	C(8)—C(9)	1·374 (7)
C(4)–N(5)	1·289 (5)	C(9)—C(10)	1·383 (6)
N(5)–C(11)	1·401 (5)	C(10)–C(11)	1·402 (5)

(*b*) Interbond angles (°)

C(2)O(1)C(10)	108·0 (3)	C(8)C(9) C(10)	119·4 (3)
O(1)C(2)N(3)	122·3 (2)	O(1)C(10)C(9)	120·1 (3)
C(2)N(3)C(4)	120·2 (3)	O(1)C(10)C(11)	118·3 (2)
N(3)C(4)N(5)	126·1 (2)	C(9)C(10)C(11)	121·6 (3)
C(4)N(5)C(11)	122·3 (3)	N(5)C(11)C(6)	118·7 (3)
C(7)C(6)C(11)	121·1 (3)	N(5)C(11)C(10)	123·6 (3)
C(6)C(7)C(8)	119·7 (3)	C(6)C(11)C(10)	117·6 (3)
C(7)C(8)C(9)	120·6 (3)		

(*c*) Torsion angles (°)

C(10)O(1)	C(2)	N(3)	+73·3 (5)
C(2) O(1)	C(10)C(11)		−65·9 (4)
O(1) C(2)	N(3) C(4)		−4·0 (6)
C(2) N(3)	C(4) N(5)		−47·7 (6)
N(3) C(4)	N(5) C(11)		+12·3 (6)
C(4) N(5)	C(11)C(10)		+33·6 (6)
O(1) C(10)C(11)N(5)			−1·3 (6)

are given in Table 1. Table 2 contains the geometrical features of the benz[*f*]-1,3,5-oxadiazepine system.* A view of one molecule, defining the atomic numbering, is shown in Fig. 1.

Discussion. Reaction of the nitrile oxides (I) (Ar = Ph, *p*-tolyl, *p*-Cl.C₆H₄ and *p*-NO₂.C₆H₄) with 2-phenyl-benzazete (II) results in the rapid discharge of the red colour of the azete and yields rearranged *yellow* 1:1 adducts. However, addition of n-pentane to the reaction solution gives a precipitate of *colourless* 1:1 adducts, which rearrange quantitatively and easily to the yellow adduct above (Rees, Somanathan, Storr & Woolhouse, 1975). Spectroscopic and other evidence suggested several plausible structures, including (VII), for the final yellow adduct, but could not unambiguously distinguish between them (Rees & Storr, 1974). We therefore undertook an X-ray analysis of the yellow 1:1 adduct resulting from the reaction of (I) (Ar = *p*-tolyl), and have proved conclusively that it possesses structure (VII). On this basis it has been postulated (Rees, Somanathan, Storr & Woolhouse, 1975) that reaction of (I) and (II) yields (III) (colourless 1:1 adducts above), (VII) being formed by the route shown. This suggestion lends independent support for the widely assumed intermediacy of oxaziridines (V) in photochemical rearrangements of heterocyclic *N*-oxides.

* A list of structure factors and a full set of dimensions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31594 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
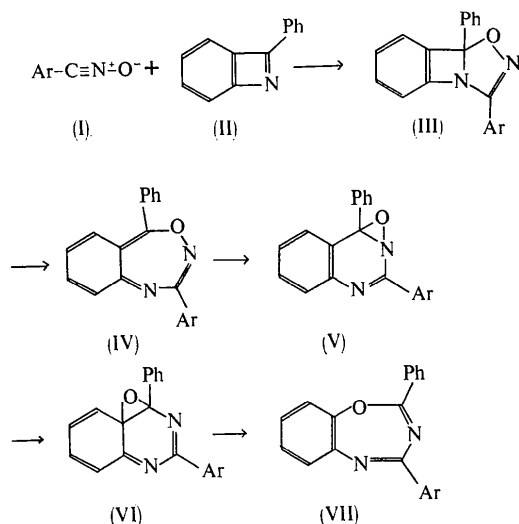
The conformation of the unusual 1,3,5-oxadiazepine ring system may be described as a distorted boat in which C(2), N(3), C(10) and C(11) form an approximately planar set with O(1) and the C(4)=N(5) double bond out-of-plane. This conformation is more exactly defined by the endocyclic torsion angles for this ring, which also indicate the distortions from more regular geometry. Thus we observe the non-zero value of the torsion angle N(3)C(4)N(5)C(11), and the non-equivalence of modular values within the pairs of torsion angles C(2)O(1)C(10)C(11) and C(10)O(1)C(2)N(3),
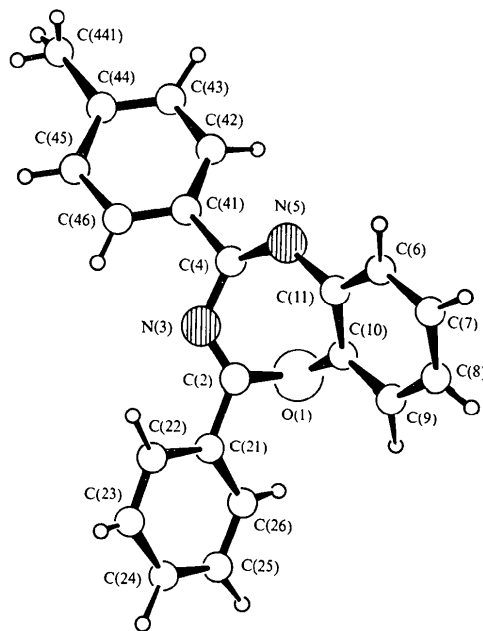

Fig. 1. A view of one molecule showing the atomic numbering; hydrogen atoms are numbered as the atoms to which they are bonded.

and C(2)N(3)C(4)N(5) and C(4)N(5)C(11)C(10). There appears, however, to be little distortion of interbond angles within this ring, the endocyclic angles at all atoms except C(4) [126·1 (2)°] differing little from those values to be expected on the basis of the bonding pattern shown in (VII).

The lengths within the oxadiazepine ring indicate that the three π-bonded systems, C(2)=N(3) [1·268 (5) Å], C(4)=N(5) [1·289 (5) Å] and the aromatic ring C(6)–C(11), are largely non-interacting, being separated by the C(4)–N(3) [1·412 (4) Å] and C(11)–N(5) [1·401 (5) Å] bonds respectively. The non-zero values of the torsion angles C(2)N(3)C(4)N(5) and C(4)N(5)C(11)C(10) support this conclusion. The difference in the lengths of C(2)=N(3) and C(4)=N(5) may possibly be considered significant, and in this respect we note two features: firstly the substituent patterns of the two bonds are different, and secondly the values of the relevant torsion angles indicate that the first bond is relatively less distorted from planarity than the second. Other dimensions within the molecule conform to accepted values for similar bond types, and there are no abnormally short intermolecular contacts.

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References

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Refinement of Sulphamic Acid

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Abstract. NH_3SO_3, $M = 97·1$. Orthorhombic, $a = 8·115$ (2), $b = 8·066$ (2), $c = 9·248$ (2) Å, $D_m = 2·14$, $Z = 8$, $D_c = 2·13$ g cm^{-3}, $F(000) = 400$. Space group *Pbca*. Mo *Kα* radiation, $\lambda = 0·7107$ Å, μ(Mo *K*) $= 8·40$ cm^{-1}. The structure has been refined by least squares to a final R of 0·027 with 793 independent diffractometer data. The length of the S–N bond is 1·772 (1) Å.

Introduction. Exposure of a small crystal to Zr-filtered Mo radiation on a Hilger & Watts Y290 diffractometer yielded 793 independent reflexions $[I \geq 2\sigma_I, \sigma_I = \sqrt{(I + B_1 + B_2)}]$, measured at room temperature by the θ, ω-scan technique in the range $2\theta = 0$–60°. From the atomic parameters derived in an earlier neutron diffraction analysis (Sass, 1960), the structure was refined by full-matrix least squares with programs incorporated in the X-RAY 72 suite of programs. Contributions from the H atoms were included in these calculations, but their positional parameters were held constant at the values (with the estimated standard deviations) determined by Sass. Isotropic thermal parameters for the H atoms were refined in later cycles. The isotropic secondary extinction coefficient (Zachariasen, 1963; Larson, 1967) was also refined in the later cycles to $g = 0·0103$. Inclusion of this parameter was observed to have a marked effect on the thermal, but not the positional parameters. At the conclusion of the refinement, the values of R and $R'(= \sum w\Delta^2/\sum w|F_o|^2)$ were 0·027 and 0·0016 respectively, the data having been weighted according to. $w = (A + B|F_o| + C|F_o|^2)^{-1}$. The final values of A, B and C were 0·3117, −0·0220 and 0·0011 respectively. The data were not corrected for absorption, and the molecular dimensions have not been corrected for the effects of thermal motion.*

Discussion. In studies of sulphonyl-stabilized imines and of sulphonium-imines, estimations of the double-bond character of the S–N bonds are frequently made by comparison of the observed lengths with that predicted from Pauling's covalent radii, 1·74 Å, or with the bond length in sulphamic acid. In the solid state the latter has the zwitterionic structure $\overset{+}{N}H_3\text{--}SO_3^-$, with, on account of the quaternary N atom, a formal S–N single bond.

Previous studies of the structure of sulphamic acid have included a two-dimensional (Kanda & King, 1951) and a three-dimensional analysis (Osaki, Tado-

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31595 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.