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# Structures of Substituted Oxadiazoles:
3-(p-Aminophenyl)-5-phenyl-1,2,4-oxadiazole

BY A. ALBINATI AND S. BRÜCKNER

Istituto di Chimica del Politecnico, 32 Piazza L. da Vinci, 20133 Milano, Italy

Abstract. $C_{14}H_{11}N_3O$, $M_r = 238.27$, monoclinic, $P2_1/c$, $Z = 4$, $a = 7.348$ (2), $b = 12.687$ (3), $c = 13.383$ (3) Å, $\beta = 105.56$ (6)° (from a least-squares refinement of 2θ values of 20 reflections), $V = 1201.89$ Å^3, $D_x = 1.32$, $D_m = 1.31$ (3) g cm^{-3}. The two phenyl rings are slightly twisted out of the plane of the oxadiazole ring in opposite directions.

Introduction. Recently, a systematic mass spectrometric study of a series of 3,5-diaryl-1,2,4-oxadiazoles (I) (Selva, Traldi, Zerilli, Cavalleri & Gallo, 1974; Selva, Traldi, Zerilli & Gallo, 1978) has been carried out to elucidate the effect of substitution on the mechanism of fragmentation of these compounds. For example, for 3,5-diphenyl-1,2,4-oxadiazole (II) a stepwise *retro* 1,3-dipolar cycloaddition has been proposed (Selva, Traldi, Zerilli & Gallo, 1976) on the basis of kinetics arguments and CNDO/2 calculations (Selva, Traldi & Fantucci, 1976). In order to test the possible extension of these arguments to other substituted oxadiazoles their detailed geometries have to be known; therefore, as part of a systematic study, we have determined the molecular structure of the title compound (III).

$$R'-C\underset{N-O}{\overset{N}{\diagdown}}C-R \qquad R = R' = C_6H_5 \text{ (II)}$$
$$R = C_6H_5; R' = C_6H_4NH_2 \text{ (III)}$$

(I)
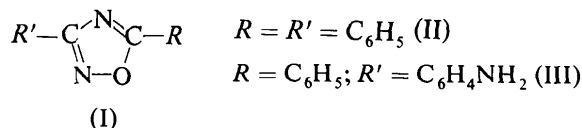
A crystal of approximate dimensions $0.25 \times 0.20 \times 0.15$ mm was obtained by slow evaporation from a methanol/n-hexane mixture.

The intensities of 2801 reflections were collected up to $2\theta = 50°$ (graphite-monochromated Mo $K\alpha$ radiation) with a Philips automated four-circle diffractometer using an $\omega/2\theta$ scan technique (scan speed $0.04°$ s^{-1}, scan range $1.1°$). For each reflection, two background counts (11 s at each side of the peak) were averaged; three standard reflections, every 60,

Table 1. *Final positional parameters* ($\times 10^4$, *for* H $\times 10^3$)

The e.s.d.'s are given in parentheses and refer to the last significant figures.

	x	y	z	B_{iso} (Å^2)
C(1)	4141 (2)	8914 (1)	8517 (2)	
C(2)	4401 (2)	8657 (1)	9564 (1)	
C(3)	5244 (2)	7723 (1)	9956 (1)	
C(4)	5877 (2)	7014 (1)	9333 (1)	
C(5)	5638 (2)	7280 (1)	8292 (1)	
C(6)	4803 (2)	8214 (1)	7894 (1)	
C(7)	6754 (2)	6019 (1)	9772 (1)	
C(8)	7844 (2)	4850 (1)	10875 (1)	
C(9)	8525 (2)	4204 (1)	11809 (2)	
C(10)	8262 (3)	4568 (1)	12735 (1)	
C(11)	8905 (3)	3969 (2)	13631 (1)	
C(12)	9784 (3)	3016 (2)	13592 (2)	
C(13)	10046 (3)	2659 (2)	12676 (2)	
C(14)	9406 (2)	3249 (1)	11777 (1)	
N(1)	7080 (2)	5777 (1)	10811 (1)	
N(2)	7277 (2)	5285 (1)	9224 (1)	
N(3)	3290 (2)	9844 (1)	8118 (1)	
O	8020 (3)	4485 (1)	9968 (1)	
H(C2)	396 (3)	914 (1)	1001 (1)	6.2 (5)
H(C3)	534 (2)	757 (1)	1064 (1)	3.9 (3)
H(C5)	607 (2)	679 (1)	786 (1)	4.8 (4)
H(C6)	470 (2)	838 (1)	718 (1)	4.2 (4)
H(C10)	762 (2)	522 (1)	1275 (1)	5.6 (4)
H(C11)	878 (3)	426 (1)	1428 (1)	6.2 (5)
H(C12)	1031 (3)	260 (2)	1424 (2)	8.5 (6)
H(C13)	1065 (3)	198 (1)	1264 (2)	6.8 (5)
H(C14)	951 (2)	300 (1)	1109 (1)	5.8 (5)
H(N3)	300 (2)	994 (1)	742 (1)	5.7 (4)
H'(N3)	278 (3)	1025 (1)	851 (2)	6.5 (5)

were measured to check the stability of the crystal and of the experimental conditions. No significant variations were observed. 1674 reflections having $I \geq 3\sigma(I)$ were considered as observed. No absorption or extinction corrections were found necessary.

The structure was solved with *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974). An *E* map calculated with the signs of the set with the highest figure of merit revealed all but the H atoms, which have been subsequently located in a difference map.

The refinement was carried out by block-diagonal least squares using anisotropic temperature factors for C, O and N, and isotropic for H; weights were chosen after Cruickshank, Pilling, Bujosa, Lovell & Truter (1961). The final *R* factor was 0·039 for the observed reflections and 0·072 with the unobserved included. The scattering factors of Cromer & Mann (1968) and, for H, of Stewart, Davidson & Simpson (1965) were used. A final difference Fourier map showed no significant features. All calculations were carried out using programs written by Immirzi (1967, 1973). The final atomic coordinates are given in Table 1 and a perspective view of the molecule showing the numbering of the atoms is given in Fig. 1.*

An analysis in terms of rigid-body motion, according to Schomaker & Trueb! ood (1968), shows that this model accounts approximately for the thermal motion; the rigid-body-corrected distances are within 2 e.s.d.'s of the uncorrected ones.

Discussion. The bond lengths are given in Fig. 1, while relevant bond angles and internal rotation angles are given in Table 2.

The entire molecule is approximately planar (the maximum deviation from planarity is 0·08 Å); the two phenyl rings are slightly twisted out of the plane of the oxadiazole ring in opposite directions, as can be judged from the values of the dihedral angles C(3)—C(4)—

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33660 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(7)—N(1) [−3·8 (2)°] and C(10)—C(9)—C(8)—N(1) [3·7 (3)°].

It has been pointed out that the substituents on a benzene ring may induce systematic deformations of the bond lengths and of the endocyclic angles (Domenicano, Vaciago & Coulson, 1975a,b; Domenicano, Mazzeo & Vaciago, 1976); correlations may also be inferred from the values of some angles and the nature of the substituent groups. The geometry found in this compound is consistent with the expected deformations; in particular, the angles C(2)—C(1)—C(6) [118·35 (7)°] and C(3)—C(4)—C(5) [118·09 (7)°] of the *para*-substituted phenyl ring are smaller than the average value of 120·0 (1)° of the unsubstituted phenyl (expected 118·4°; Domenicano et al., 1976).

The C(2)—C(3) and C(5)—C(6) bond lengths [ave. 1·373 (3) Å] are again shorter than the mean of 1·386 (±0·009) Å, thus lowering the ideal D_{6h} symmetry.

The C—N(3) distance of 1·375 (3) Å is in the usual range found in *p*-amino-substituted benzene [*e.g.* 1·360 (4) Å in 2-(4,4-dimethylanilino)-4-phenyl-6a-thiathiophthene; Hardvik & Sæthre, 1972].

The other phenyl ring does not show any particular feature, with averages of 1·381 (3) Å for C—C distances and 120·00 (±0·04)° for the angles.
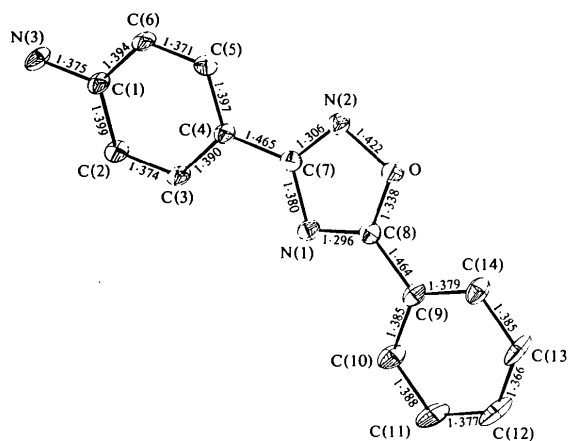

Fig. 1. An *ORTEP* drawing (Johnson, 1965) of the molecule, showing the numbering of the atoms and the bond lengths. All the values are in Å and the associated e.s.d.'s are $\sigma = 0.003$ Å.

Table 2. *Bond angles* (°) *and internal rotation angles* (°)

C(1)—C(2)—C(3)	120·54 (8)	C(9)—C(10)—C(11)	119·48 (9)	N(3)—C(1)—C(2)	120·87 (8)
C(1)—C(6)—C(5)	120·74 (7)	C(9)—C(14)—C(13)	119·91 (10)	N(3)—C(1)—C(6)	120·77 (7)
C(2)—C(1)—C(6)	118·35 (7)	C(10)—C(9)—C(14)	120·11 (8)	O—C(8)—C(9)	119·08 (7)
C(2)—C(3)—C(4)	121·22 (7)	C(10)—C(11)—C(12)	120·03 (11)	O—C(8)—N(1)	113·69 (6)
C(3)—C(4)—C(5)	118·09 (7)	C(11)—C(12)—C(13)	120·38 (10)	O—N(2)—C(7)	103·37 (5)
C(3)—C(4)—C(7)	119·93 (6)	C(12)—C(13)—C(14)	120·08 (9)		
C(4)—C(5)—C(6)	121·03 (8)	N(1)—C(7)—N(2)	114·23 (7)	C(2)—C(1)—N(3)—H(N3)	−172·0 (2)
C(5)—C(4)—C(7)	121·98 (7)	N(1)—C(7)—C(4)	122·17 (7)	C(3)—C(4)—C(7)—N(1)	−3·8 (2)
C(7)—N(1)—C(8)	102·76 (7)	N(1)—C(8)—C(9)	127·22 (8)	C(3)—C(4)—C(7)—N(2)	−175·6 (3)
C(8)—C(9)—C(10)	118·62 (8)	N(2)—C(7)—C(4)	123·60 (7)	C(10)—C(9)—C(8)—N(1)	3·7 (3)
C(8)—C(9)—C(14)	121·28 (9)	N(2)—O—C(8)	105·95 (5)	C(10)—C(9)—C(8)—O	177·3 (2)

The mean C—H distance for the benzene rings is 0·97 ($\pm$0·02) Å.

The oxadiazole ring is planar and shows a certain amount of shortening of bond lengths, consistent with some aromatic nature. For example, it is interesting to note that the C(7)—N(1) bond |1·380 (3) Å| is shorter than the average value of 1·475 Å reported for the C—N bond, when N is sp^2 hybridized (Sutton, 1965). On the other hand, the above-mentioned bond is comparable with the length of 1·369 Å in other aromatic compounds, like some substituted purines (Glusker, van der Helm, Lowe, Minkin & Patterson, 1968), or 1·383 (4) Å in pyrrole (Sutton, 1965).

The same trend is also evident in the C(8)—O bond which is consistent with those of similar compounds, e.g. 1·353 (7) Å in 3-hydroxy-5-phenylisoxazole (Biagini, Cannas & Marongiu, 1969).

If the lengths of C(7)—C(4) and C(8)—C(9) |ave. 1·464 (3) Å| are compared with those of sp^2-hybridized C atoms |e.g. 1·497 (2) Å in biphenyl; Robertson, 1961|, a certain degree of conjugation between rings may be assumed by analogy with other phenyl-substituted isoxazoles where distances in the range 1·44–1·47 Å have been found (Biagini et al., 1969).

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The Structure of Dimethylammonium Dimethyldithiocarbamate

BY ANDERS WAHLBERG

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden

Abstract. $[(CH_3)_2NH_2]^+[(CH_3)_2NCS_2]^-$, monoclinic, $P2_1/c$, $a = 9·979$ (3), $b = 7·701$ (1), $c = 12·189$ (3) Å, $\beta = 105·81$ (2)°, $Z = 4$, $V = 901·2$ Å^3, $D_m = 1·225$ (flotation), $D_x = 1·226$ g cm^{-3}. The structure has been solved by direct methods and refined by full-matrix least squares. $R(F^2) = 0·053$ for 1964 reflexions and 138 varied parameters. The ordered structure is built up of one-dimensional zig-zag chains along b. Each molecular ion is involved in four intermolecular H—S interactions between the ammonium protons and the dithiocarbamate S atoms, at H—S distances of 2·46 (3), 2·61 (3), 2·66 (3) and 2·99 (3) Å.