

**The Structures of Two Condensation Products of Dithizone.
2-Methyl-3-phenyl-5-phenylazo-1,3,4-thiadiazoline and 5,6-Dihydro-4-phenyl-2-phenylazo-4*H*-1,3,4-thiadiazine**

BY PAMELA A. MCCALLUM, HARRY M. N. H. IRVING, ALAN T. HUTTON AND LUIGI R. NASSIMBENI*

School of Chemical Sciences, University of Cape Town, South Africa

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Abstract

2-Methyl-3-phenyl-5-phenylazo-1,3,4-thiadiazoline (I) crystallizes in space group $P2_1$ with $a = 12.238$ (6), $b = 6.660$ (3), $c = 9.034$ (5) Å, $\beta = 96.4$ (2)°, $Z = 2$. 5,6-Dihydro-4-phenyl-2-phenylazo-4*H*-1,3,4-thiadiazine (II) crystallizes in space group $P2_1/c$ with $a = 9.940$ (5), $b = 8.914$ (4), $c = 16.448$ (8) Å, $\beta = 102.9$ (2)°, $Z = 4$. The structures were refined to a final R of 0.049 and 0.044 respectively. Electron delocalization within the Ph–N=N–C=N–N–Ph chain results in essentially planar molecules. (I) is an example of spontaneous resolution from a racemic mixture.

Introduction

Dithizone (1,5-diphenylthiocarbazone) is an important analytical reagent in trace-metal analysis, forming stable complexes with several metal cations. The compound does, however, suffer the disadvantage that its solutions deteriorate with time, the rate of decomposition increasing with pH and temperature and being accelerated by aeration and the presence of catalytic amounts of various metals. From the large literature on dithizone (Irving, 1977), there is strong support for the assumption that deteriorated solutions of dithizone contain more than one product, and that these may not even be the same in different solvents. Indeed, traces of aldehydes and ketones often present in otherwise pure and redistilled solvents can condense with dithizone to give yellow solutions of thiadiazolines (Irving & Mahnot, 1967, 1968). 2-Methyl-3-phenyl-5-phenylazo-1,3,4-thiadiazoline (I) is such a condensation product, the reaction occurring between dithizone and acetaldehyde. In this paper, its structure is compared with that of the homologue, 5,6-dihydro-4-phenyl-2-phenylazo-4*H*-1,3,4-thiadiazine (II), in which the heterocyclic ring is expanded from five to six members.

Experimental

(I) was prepared by the method of Irving & Mahnot (1968) and recrystallized from ethanol to yield dark red needles elongated along b . (II) was prepared by a modification of the method of Neugebauer & Fischer (1974) and recrystallized from ethanol to give yellow lozenge-shaped crystals.

The lattice constants were obtained by least squares from the settings of 25 reflections measured on a four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). During data collection three reference reflections were periodically monitored. Crystal data and experimental details are listed in Table 1. The data were corrected for Lorentz–polarization effects but not for absorption.

Solution and refinement of the structures

The structure of (I) was solved by weighted multi-solution tangent refinement (Germain, Main & Woolfson, 1971) with *SHELX* (Sheldrick, 1978). A starting set of reflections was selected and used to generate 256 phase permutations, and after weighted tangent refinement for each, ten E maps were produced. Several of these appeared to show the positions of most of the heavy atoms, but attempts at refinement of the structure based on these positions all failed. Further inspection of the E maps, however, showed that each map gave two shifted molecules and care was taken to apply an appropriate vector shift, perpendicular to the 2_1 axis, and thus find the correct average structure (Caira, Giles, Nassimbeni, Sheldrick & Hazell, 1976; Hazell & Hazell, 1975). This yielded all but six of the heavy atoms which were found in subsequent difference maps. In the final refinement the heavy atoms were treated anisotropically. The H atoms were constrained to be 1.08 Å from their corresponding C atoms, their positions being dictated by the geometry of the molecule. Their isotropic temperature factors were treated as three single parameters

* Author to whom correspondence should be addressed.

whose final values are reported in Table 1, which also gives other relevant refinement parameters.

The structure of (II) was solved by the automatic centrosymmetric subroutine of *SHELX* (Sheldrick, 1978) in which an *E* map yielded the positions of all the

heavy atoms. The subsequent refinement was carried out as for (I) and the important parameters are listed in Table 1. Table 2 gives the final atomic coordinates for (I) and (II).*

Table 1. *Crystal data and experimental and refinement parameters for the crystal structures of (I) and (II)*

Crystal data	(I)	(II)
Molecular formula	C ₁₅ H ₁₄ N ₂ S	C ₁₅ H ₁₄ N ₂ S
Composition	C H N	C H N
Found (%)	63.4 5.0 19.9	63.6 5.0 19.7
Calculated (%)	63.8 5.0 19.8	63.8 5.0 19.8
Melting point (K)	371–372 decomp.	422–423 decomp.
<i>M_r</i>	282.4	282.4
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	12.238 (6)	9.940 (5)
<i>b</i> (Å)	6.660 (3)	8.914 (4)
<i>c</i> (Å)	9.034 (5)	16.448 (8)
β (°)	96.4 (2)	102.9 (2)
<i>V</i> (Å ³)	731.72	1420.38
<i>D_m</i> (Mg m ⁻³)	1.25	1.30
<i>D_c</i> (Mg m ⁻³)	1.28 for <i>Z</i> = 2	1.32 for <i>Z</i> = 4
μ (Mo <i>K</i> α) (mm ⁻¹)	0.18	0.18
<i>F</i> (000)	296	592
Data collection		
Crystal dimensions (mm)	0.08 × 0.20 × 0.33	0.15 × 0.50 × 0.53
Scan mode	ω -2 θ	ω -2 θ
Scan width (° θ)	1.2	1.2
Scan speed (° θ s ⁻¹)	0.04	0.04
Range scanned (2 θ) (°)	6–46	6–44
Stability of standard reflections (%)	0.9	1.4
Number of reflections collected	1118	1878
Number of observed reflections	785 with <i>I</i> (rel) > 2 σ <i>I</i> (rel)	1413 with <i>I</i> (rel) > 2 σ <i>I</i> (rel)
Final refinement		
Number of variables	188	183
$R = \sum F_o - F_c / \sum F_o $	0.049	0.044
$R_w = \sum w^{1/2} F_o - F_c / \sum w^{1/2} F_o $	0.039	0.047
Weighting scheme <i>w</i>	($\sigma^2 F$) ⁻¹	($\sigma^2 F + 7.39 \times 10^{-4} F^2$) ⁻¹
<i>U</i> (methine H) (Å ²)	0.100	—
<i>U</i> (methyl H) (Å ²)	0.168	—
<i>U</i> (methylene H) (Å ²)	—	0.089
<i>U</i> (aromatic H) (Å ²)	0.100	0.084

Description of the structures and discussion

Perspective views of the molecules of (I) and (II) are shown in Figs. 1 and 2 respectively. An arbitrary numbering scheme has been employed in order to facilitate comparison of relevant molecular parameters of the two structures. The bond lengths, bond angles and selected torsion angles are shown in Figs. 3, 4 and 5 respectively. The bond lengths show considerable π -electron delocalization within the N=N=C=N-N chain and with the phenyl rings. Thus, for (I) and (II), the formal single bonds N(8)–C(9) [1.382 (7), 1.408 (3) Å] and N(10)–N(11) [1.355 (7), 1.344 (3) Å] are shortened, while the formal double bond N(7)=N(8) [1.270 (5), 1.264 (3) Å] is lengthened in comparison with accepted standard values (Kennard, 1962). The C(9)=N(10) lengths [1.283 (7), 1.290 (3) Å] are more difficult to compare, there being no readily available accepted value for C=N, although Burke-Laing & Laing (1976) estimate 1.27 Å. This π -electron delocalization effect has been noted in related structures, e.g. 3-carboxymethylthio-1,5-diphenylformazan (Hutton, Irving, Nassimbeni & Gafner, 1979), 3-

* Lists of anisotropic temperature factors, hydrogen-atom coordinates and structure factors for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35178 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates (× 10⁴) of the heavy atoms*

	(I)			(II)		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
S	7563 (2)	8752 (0)	6326 (2)	2351 (1)	1065 (1)	1050 (1)
C(1)	9852 (5)	13435 (14)	7536 (7)	2735 (3)	–3001 (3)	–112 (2)
C(2)	9960 (6)	15263 (13)	6876 (8)	1936 (3)	–4300 (3)	–176 (2)
C(3)	10754 (6)	16618 (14)	7490 (8)	2247 (4)	–5485 (4)	–642 (2)
C(4)	11444 (7)	16029 (19)	8737 (9)	3344 (4)	–5389 (5)	–1033 (2)
C(5)	11342 (7)	14213 (17)	9411 (8)	4152 (4)	–4108 (4)	–952 (2)
C(6)	10547 (5)	12858 (14)	8806 (7)	3850 (3)	–2912 (4)	–487 (2)
N(7)	9059 (4)	11970 (9)	7008 (5)	2482 (2)	–1681 (3)	320 (1)
N(8)	8409 (4)	12543 (9)	5895 (6)	1344 (2)	–1693 (3)	542 (1)
C(9)	7631 (6)	11105 (11)	5436 (7)	1121 (3)	–371 (3)	962 (2)
N(10)	6880 (5)	11479 (9)	4363 (6)	–7 (2)	–415 (2)	1226 (1)
N(11)	6163 (4)	9930 (11)	4142 (6)	–378 (2)	701 (3)	1679 (1)
C(12)	5308 (5)	10050 (13)	2962 (7)	–1655 (3)	520 (3)	1901 (2)
C(13)	4516 (5)	8556 (14)	2791 (6)	–1955 (3)	1276 (4)	2576 (2)
C(14)	3644 (5)	8744 (15)	1670 (7)	–3245 (3)	1129 (4)	2758 (2)
C(15)	3573 (6)	10345 (17)	735 (7)	–4235 (3)	219 (4)	2285 (2)
C(16)	4351 (5)	11835 (13)	912 (7)	–3937 (3)	–555 (4)	1623 (2)
C(17)	5226 (5)	11685 (12)	2016 (7)	–2658 (3)	–421 (3)	1425 (2)
C(18)	6558 (6)	7966 (12)	4781 (8)	516 (3)	1987 (4)	1979 (2)
C(19)	7092 (7)	6688 (13)	3664 (8)	1284 (3)	2501 (4)	1340 (2)

methylthio-1,5-diphenylformazan (Preuss & Gieren, 1975), 3-methylthio-1,5-di(*o*-tolyl)formazan (Hutton, Irving & Nassimbeni, 1980), in dithizone itself (Laing, 1977), as well as in its metal complexes, *e.g.* methyl- and phenylmercury(II) dithizonates (Hutton, Irving, Nassimbeni & Gafner, 1980).

The molecules of (I) and (II) are roughly planar, as shown by the torsion angles calculated for the Ph-N=N-C=N-N-Ph chain and by Fig. 6 which gives an edge-on view of (I). The S-C lengths are within accepted values, as are the remaining C-C lengths in both structures. The conformation of the thiol rings in the molecules can be seen on examination of Fig. 5 which gives the endocyclic torsion angles. These conformations are described both in terms of asymmetry parameters (Duax & Norton, 1975) and parameters of pucker. In the latter method (Boeyens, 1978), parameters of pucker for five- and six-membered rings are obtained in the form of polar coordinates (Cremer & Pople, 1975). The total degree of pucker is characterized by the radial coordinate Q , and the angular coordinates θ and φ (six-membered rings) or φ (five-membered rings) detail the shape of the ring. Both sets of conformational parameters are given in Table 3.

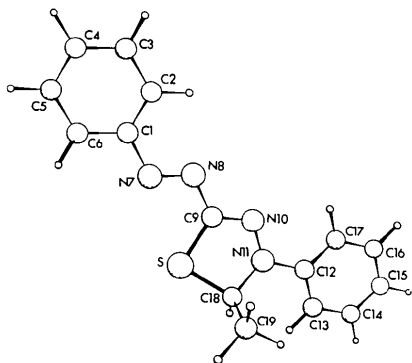


Fig. 1. The molecular structure of (I), with atomic nomenclature.

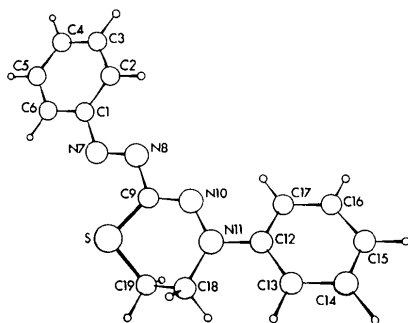


Fig. 2. The molecular structure of (II), with atomic nomenclature.

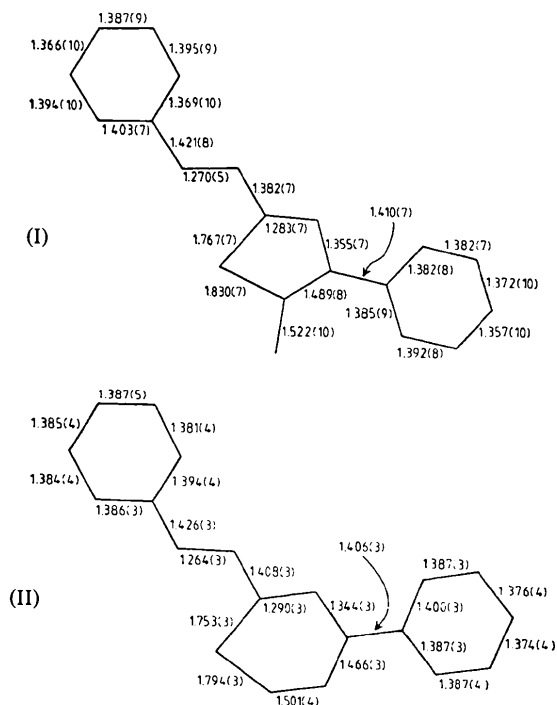


Fig. 3. Principal bond lengths (Å).

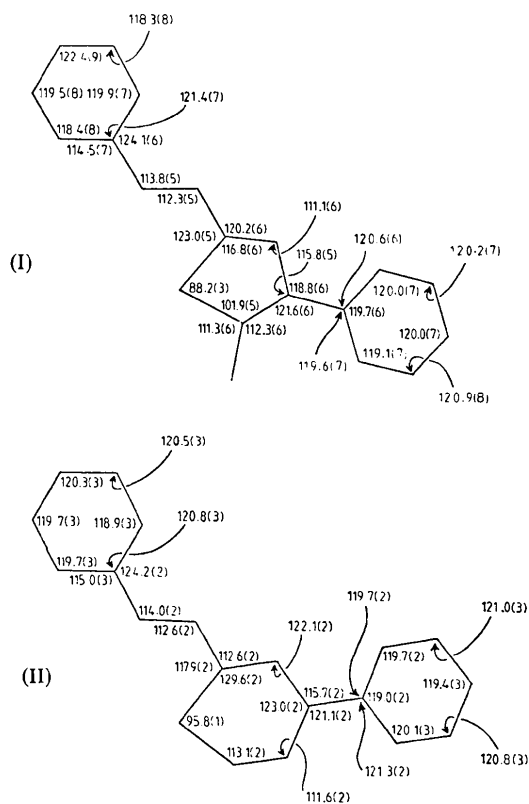


Fig. 4. Principal bond angles (°).

The packing in the structures is shown in Figs. 7 and 8. The packing densities (defined as the mean volume per non-hydrogen atom) are normal, but the packing in (I) (18.3 \AA^3) is slightly looser than that in (II) (17.8 \AA^3). This is attributed to the projecting methyl group of (I). There are no significant intermolecular close contacts.

An interesting feature of (I) is that it crystallizes in the non-centrosymmetric space group $P2_1$, thus requiring that all the molecules in a crystal be of the same chirality. Upon optical analysis, the crystals did not reveal hemihedral faces and could not therefore be differentiated. The solution from which the crystals were grown showed no optical activity and we therefore conclude that this is another example of spontaneous resolution occurring upon crystallization of a racemic mixture. Other examples have been reported by Cheng, Koo, Mellor, Nyburg & Young (1970), Larsen (1972), Chieh (1978) and Secor (1963).

All calculations were carried out on a Univac 1100/81 computer at the University of Cape Town.

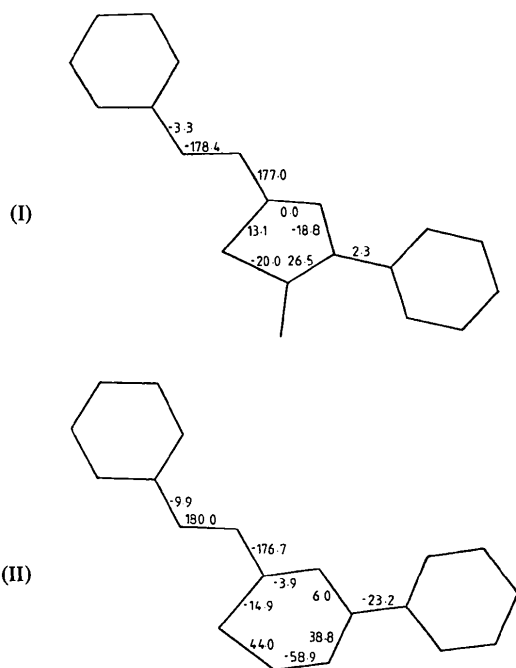


Fig. 5. Selected torsion angles ($^\circ$), illustrating the planarity of the structures. E.s.d.'s are $ca 0.6^\circ$ for (I) and $ca 0.4^\circ$ for (II).

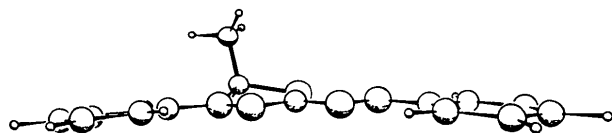


Fig. 6. An edge-on view of (I).

Table 3. Thiol ring conformations

(a) Parameters of pucker	Q (\AA)	ϕ ($^\circ$)	θ ($^\circ$)	3E $E_0: {}^3H_6$ (2:1)
(I) S-C(9)-N(10)-N(11)-C(18)	0.26	146	-	
(II) S-C(9)-N(10)-N(11)-C(18)-C(19)	0.39	288	53	

(b) Asymmetry parameters showing dominant symmetry	Envelope
(I) $\Delta C_1C(18) = 6.1^\circ$	Envelope
(II) $\Delta C_1N(10) = 16.3^\circ$	Envelope

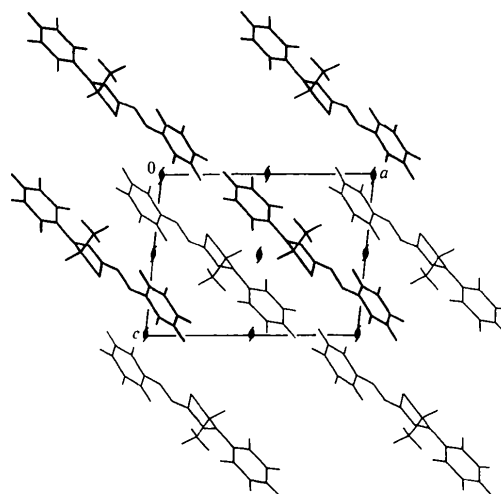


Fig. 7. A projection of the structure of (I) along b .

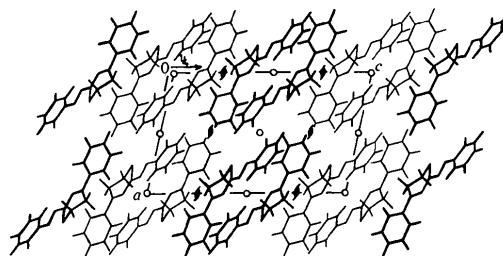


Fig. 8. A projection of the structure of (II) along b .

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