p-Carboxyphenylazoxycyanide–Dimethyl Sulphoxide: an Antibacterial and Antifungal Compound from *Calvatia lilacina*

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Abstract. $C_8H_5N_3O_3 . C_2H_6OS$, monoclinic, $P2_1/a$, $a = 23.19(2)$, $b = 6.96(1)$, $c = 7.65(1)$ Å, $\beta = 96.98(5)°$, $Z = 4$, $D_c = 1.46$ g cm^{-3}. The proposed structure of the title compound has been confirmed, with the oxygen atom in the azoxy group bonded to the nitrogen adjacent to the benzene ring and with an *anti* orientation of the phenyl and cyano groups. The carboxyl group is connected to a molecule of dimethyl sulphoxide by a rather short hydrogen bond.

Introduction. Yellow crystals (m.p. 164–165 °C in glass capillary), containing one molecule of solvent per asymmetric unit, were obtained by crystallization from dimethyl sulphoxide. The sample contained both twinned prismatic and non-twinned plate-like crystals. Systematic absences indicate space group $P2_1/a$. Approximate cell dimensions were obtained from Weissenberg photographs and refined by least-squares cal-culations on diffractometer data. The intensities of 1674 independent reflexions were collected on a Philips four-circle automatic diffractometer equipped with a graphite monochromator, using the θ–2θ scanning technique and Mo $K\alpha$ radiation; 460 reflexions with $I \geq 2\sigma(I)$ were considered to be unobserved and not used in the refinement of the structure. The intensities were corrected for Lorentz and polarization effects but not for absorption or extinction. The structure was solved by direct methods with the *MULTAN* procedure (Declerq, Germain, Main & Woolfson, 1973). With 200 normalized structure factors ($E_{min} = 1.61$) and 2000 $\sum_2$ relationships, eight sets of phases were generated. The map computed with the most consistent set showed all 18 non-hydrogen atoms. The least-squares refinement of the structure was initially by block-diagonal methods (with unit weights) and, in the final stages, by full-matrix methods. All hydro-

Table 1. *Atomic coordinates and temperature factors*

Standard errors are shown in parentheses. The anisotropic temperature factors were calculated from
$$\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*) \right].$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	0·2056 (1)	0·8620 (3)	0·6164 (2)	4·89 (9)	6·02 (11)	5·16 (9)	−0·08 (4)	0·07 (3)	0·15 (4)
O(1)	0·1435 (2)	0·8912 (8)	0·6465 (7)	4·4 (2)	6·9 (3)	7·7 (3)	0·0 (1)	0·2 (1)	0·9 (1)
O(2)	0·1397 (2)	0·3174 (8)	0·9453 (8)	4·3 (2)	5·8 (3)	10·4 (4)	−0·3 (1)	−0·4 (1)	0·8 (1)
O(3)	−0·0720 (2)	0·9026 (7)	0·5459 (7)	5·3 (2)	4·9 (3)	8·1 (3)	0·1 (1)	−0·3 (1)	1·0 (1)
O(4)	−0·1395 (2)	0·6795 (8)	0·5550 (8)	4·7 (3)	7·2 (3)	9·3 (4)	−0·1 (1)	−0·2 (1)	0·8 (1)
N(1)	0·1536 (2)	−0·1234 (10)	1·1102 (9)	5·9 (3)	5·5 (3)	7·9 (4)	0·5 (1)	0·2 (1)	0·6 (2)
N(2)	0·0753 (2)	0·0846 (9)	0·9581 (8)	5·0 (3)	4·6 (3)	6·6 (3)	0·2 (1)	0·2 (1)	0·7 (1)
N(3)	0·0904 (2)	0·2550 (8)	0·9168 (7)	3·7 (3)	5·0 (3)	5·4 (3)	−0·1 (1)	0·3 (1)	0·0 (1)
C(1)	0·2252 (4)	0·6465 (15)	0·7287 (13)	7·3 (5)	7·9 (6)	8·7 (5)	0·7 (2)	−0·2 (2)	0·1 (2)
C(2)	0·2462 (3)	1·0270 (13)	0·7547 (13)	5·5 (4)	6·4 (5)	10·6 (6)	−0·5 (2)	0·7 (2)	−0·7 (2)
C(3)	0·1207 (3)	−0·0190 (11)	1·0419 (9)	4·0 (3)	5·1 (4)	6·0 (4)	0·0 (1)	0·5 (1)	0·1 (2)
C(4)	0·0434 (3)	0·3750 (10)	0·8288 (8)	4·8 (3)	4·1 (3)	4·3 (3)	−0·2 (1)	0·2 (1)	−0·1 (1)
C(5)	−0·0117 (3)	0·3004 (10)	0·7927 (9)	4·6 (3)	4·8 (3)	5·9 (4)	−0·3 (1)	0·0 (1)	0·5 (1)
C(6)	−0·0544 (3)	0·4218 (11)	0·7127 (9)	4·2 (3)	5·6 (4)	6·0 (4)	−0·4 (1)	0·2 (1)	0·0 (2)
C(7)	−0·0417 (3)	0·6082 (10)	0·6728 (8)	4·2 (3)	4·3 (3)	4·5 (3)	−0·2 (1)	0·3 (1)	−0·2 (1)
C(8)	0·0138 (3)	0·6794 (10)	0·7088 (9)	4·8 (3)	4·1 (3)	6·0 (3)	0·0 (1)	0·1 (1)	−0·3 (1)
C(9)	0·0583 (3)	0·5597 (11)	0·7882 (9)	4·4 (3)	4·9 (3)	5·7 (3)	−0·2 (1)	0·0 (1)	0·1 (1)
C(10)	−0·0893 (3)	0·7321 (10)	0·5854 (9)	4·3 (3)	4·6 (3)	5·1 (3)	0·1 (1)	0·4 (1)	0·2 (1)

	x	y	z	B		x	y	z	B
H(3)	0·107 (3)	1·012 (11)	0·526 (9)	6 (2)	H(12)	0·219 (3)	0·678 (10)	0·860 (8)	4 (2)
H(5)	−0·020 (3)	0·175 (9)	0·821 (8)	3 (1)	H(13)	0·203 (3)	0·570 (12)	0·667 (9)	6 (2)
H(6)	−0·089 (3)	0·368 (10)	0·684 (8)	3 (1)	H(21)	0·292 (3)	0·999 (11)	0·754 (8)	4 (2)
H(8)	0·025 (3)	0·817 (10)	0·684 (9)	3 (1)	H(22)	0·232 (3)	0·963 (11)	0·861 (9)	5 (2)
H(9)	0·095 (3)	0·606 (9)	0·824 (8)	3 (1)	H(23)	0·231 (3)	1·149 (11)	0·746 (10)	6 (2)
H(11)	0·261 (3)	0·642 (10)	0·717 (9)	4 (2)					

gen atoms were located on a difference Fourier map and refined isotropically. With anisotropic thermal parameters assigned to all other atoms, the final conventional R value was 0·076 (R=0·101 for all 1674 reflexions). The weighting scheme introduced in the late stages of the refinement was: $w = 1/\{1 + [(|F_o| - B)/A]^2\}$, with $A = 18\cdot0$ and $B = 6\cdot0$.

Fig. 1 shows the atomic numbering scheme on a projection of the molecule onto its mean plane. Atomic coordinates and temperature factors are given in Table 1 and bond distances and angles in Table 2.*

Discussion. The structure of an antibacterial and antifungal compound isolated from the culture broth of *Calvatia lilacina* (Berk.) Henn. P. has been described (Gasco, Serafino, Mortarini, Menziani, Bianco & Ceruti Scurti, 1974) on the basis of chemical and spectroscopic studies as *p*-carboxyphenylazoxycyanide (I):

N
‖
C
‖
N
|
O、、N
|
(benzene ring)
|
COOH

(I)
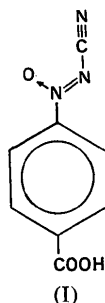
* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31035 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Two problems remained: The exact stereoisomerism of the compound could not be confirmed experimentally at that stage and the position of the oxygen atom in the azoxycyano group could only be assigned, with some uncertainty, on the basis of a similar assignment
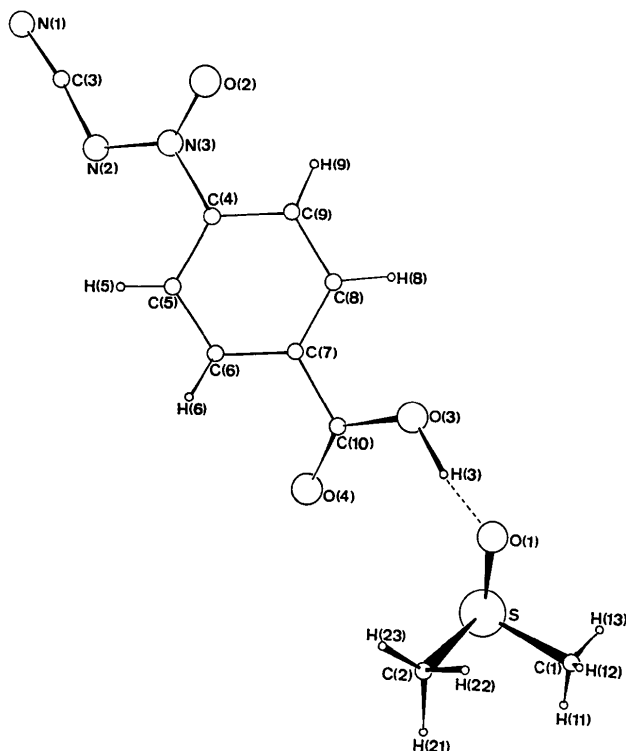

Fig. 1. Projection of the molecule onto its mean plane.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with standard errors in parentheses*

N(1)–C(3)	1·134 (10)	C(6)—H(6)	0·89 (6)	S——O(1)	1·499 (5)
N(2)–C(3)	1·369 (9)	C(7)—C(8)	1·375 (9)	S——C(1)	1·761 (10)
N(2)–N(3)	1·287 (8)	C(7)—C(10)	1·493 (9)	S——C(2)	1·756 (9)
N(3)–O(2)	1·218 (7)	C(8)—C(9)	1·406 (9)	C(1)–H(11)	0·85 (7)
C(4)–N(3)	1·471 (8)	C(8)—H(8)	1·01 (7)	C(1)–H(12)	1·05 (7)
C(4)–C(5)	1·374 (9)	C(9)—H(9)	0·92 (6)	C(1)–H(13)	0·84 (7)
C(4)–C(9)	1·376 (10)	C(10)–O(3)	1·300 (9)	C(2)–H(21)	1·09 (7)
C(5)–C(6)	1·387 (10)	C(10)–O(4)	1·215 (8)	C(2)–H(22)	1·01 (8)
C(5)–H(5)	0·93 (7)	O(3)–H(3)	1·11 (7)	C(2)–H(23)	0·92 (8)
C(6)–C(7)	1·373 (10)	O(1)–H(3)	1·44 (7)		

N(1)–C(3)–N(2)	171·5 (8)	C(6)—C(7)—C(10)	118·6 (6)	O(1)—S——C(2)	105·9 (4)
C(3)–N(2)–N(3)	112·6 (6)	C(8)—C(7)—C(10)	120·3 (6)	C(1)—S——C(2)	100·1 (4)
N(2)–N(3)–C(4)	115·3 (5)	C(7)—C(8)—C(9)	119·5 (6)	S——C(1)-H(11)	100 (5)
N(2)–N(3)–O(2)	124·2 (6)	C(7)—C(8)—H(8)	124 (4)	S——C(1)-H(12)	104 (4)
O(2)–N(3)–C(4)	120·5 (6)	C(9)—C(8)—H(8)	117 (4)	S——C(1)-H(13)	99 (5)
N(3)–C(4)–C(5)	119·7 (6)	C(8)—C(9)—C(4)	117·4 (6)	H(11)–C(1)–H(12)	110 (6)
N(3)–C(4)–C(9)	116·2 (5)	C(8)—C(9)—H(9)	122 (4)	H(11)–C(1)–H(13)	117 (7)
C(5)–C(4)–C(9)	124·1 (6)	C(4)—C(9)—H(9)	121 (4)	H(12)-C(1)–H(13)	122 (6)
C(4)–C(5)–C(6)	117·1 (7)	C(7)—C(10)–O(3)	113·5 (6)	S——C(2)-H(21)	110 (4)
C(4)–C(5)–H(5)	121 (4)	C(7)—C(10)–O(4)	123·4 (6)	S——C(2)-H(22)	90 (4)
C(6)–C(5)–H(5)	121 (4)	O(3)—C(10)–O(4)	123·1 (6)	S——C(2)-H(23)	113 (4)
C(5)–C(6)–C(7)	120·9 (6)	C(10)–O(3)—H(3)	112 (4)	H(21)-C(2)–H(22)	109 (5)
C(5)–C(6)–H(6)	115 (4)	O(3)—H(3)—O(1)	167 (7)	H(21)-C(2)–H(23)	123 (6)
C(7)–C(6)–H(6)	124 (4)	O(1)—S——C(1)	103·7 (4)	H(22)-C(2)–H(23)	108 (7)
C(6)–C(7)–C(8)	121·1 (6)				

proposed by Angeli (1917,* 1930) and Pieroni (1922) for phenylazoxycarbonamides. The present analysis represents the first X-ray structure determination of an azoxycyano derivative and was undertaken in order to provide an unambiguous answer to these questions. The results are in agreement with the predictions of Gasco *et al.* (1974) as far as the position of the oxygen atom in the azoxycyano group is concerned; O(2) is actually bonded to the nitrogen atom adjacent to the benzene ring. The N(3)–O(2) distance is very short when compared with those found in azoxy compounds [1·279 Å in *p*-azoxyanisole (Krigbaum, Chatani & Barber, 1970), 1·291 Å in ethyl *p*-azoxybenzoate (Krigbaum & Barber, 1971)] and is of the same order as the N–O bonds in nitro groups or furoxans. The relative *anti* orientation of the benzene ring and the cyano group is confirmed. The geometry of the diazocyano group is similar to that found in *p*-chloro- (Gram & Rømming, 1967) and in *o*-bromobenzene-*anti*-diazocyanide (Bø, Klewe & Rømming, 1971), with the exception of the C(4)–N(3) distance which is longer in our case (1·471 compared with 1·403 Å in the more accurately determined *o*-bromo compound). The structure of the DMSO solvate presents no exceptional feature when compared with the structure of DMSO alone (Thomas, Shoemaker & Eriks, 1966). The molecule of DMSO is connected to the carboxyl group of the carboxyphenylazoxycyanide moiety by a rather strong hydrogen bond O–H···O of 2·526(7) Å. The

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* And other papers in the series.

molecule of *p*-carboxyphenylazoxycyanide as a whole is only roughly planar, whereas the three separate azoxycyanide, phenyl and carboxyl [including C(7)] groups show no significant deviation from planarity. The dihedral angle between the carboxyl and the phenyl planes is 2·6° as a consequence of a slight rotation about the C(7)–C(10) bond. The azoxycyanide group forms an angle of 2·8° with the benzene ring owing to a folding at C(4) and a slight rotation about C(4)–N(3).

No short intermolecular contacts exist and the packing of the molecules in the crystal is due to van der Waals interactions only.

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1-Methyl-4-thiouracil

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Abstract. $C_5H_6N_2OS$, monoclinic, $P2_1/c$, $a=6\cdot757(1)$, $b=13\cdot618(2)$, $c=7\cdot010(1)$ Å, $\beta=99\cdot36(1)°$, $Z=4$, $D_c=1\cdot484$, $D_m=1\cdot488$ g cm^{-3}, $V=636\cdot45$ Å^3, F.W. 142·2, $\lambda(\mathrm{Cu}\ K\alpha_1)=1\cdot5405$ Å, $\mu=36\cdot7$ cm^{-1}, $F(000)=296$. The intensity data were collected on an automated diffractometer and the structure was solved by the heavy-atom technique. Full-matrix least-squares refinement yielded an R of 0·033 for 978 reflections. The molecules form dimers in the crystal *via* N(3)–H(3)···S hydrogen bonds (N–S distance 3·328 Å). The crystal structure is similar to that of the more stable form of 1-methylthymine [Hoogsteen, *Acta Cryst.* (1963). **16**, 28–38].

Introduction. 1-Methyl-4-thiouracil has been used in chemical studies as a model of the nucleoside 4-thiouridine (Pal, Uziel, Doherty & Cohn, 1969), and in a crystallographic study of the hydrogen-bonded base pair with 9-methyladenine (Saenger & Suck, 1971*a*). The importance of considering N–H···S hydrogen bonds in nucleic acid structures has been emphasized

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