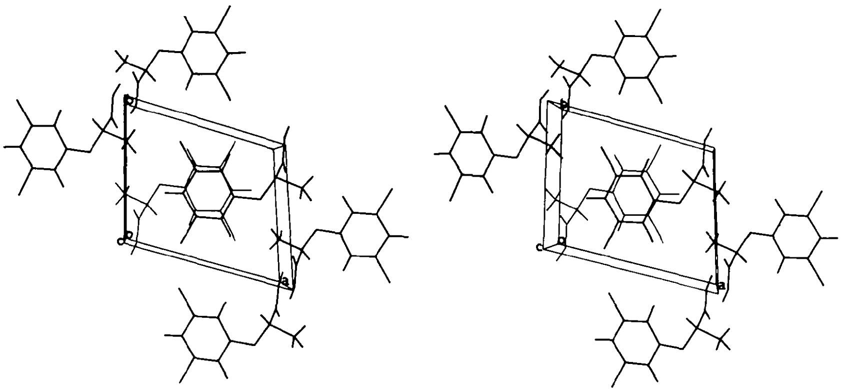

Fig. 2. Stereoview perpendicular to the *ab* plane.

tation, resulting in the synplanar conformation, was determined by the non-bonded interactions between H atoms on the β-C and the carbonyl O. The C—O(carbonyl) and C—O(hydroxyl) distances [1·237 (6) and 1·276 (7) Å respectively] are significantly different from the mean values of 1·21 and 1·31 Å (Leiserowitz, 1976) for dimeric carboxylic acids. The only other member of the phenoxy series to exhibit a similar effect is 2,4,6-T [1·235 (5) and 1·262 (5) Å] (Smith, Kennard & White, 1977) which is also symmetrically substituted and is herbicidally inactive. This phenomenon suggests partial orientational disorder of the carboxyl group as a result of the intermolecular environment of the carboxyl dimer.

The molecules pack in the cell with the planes of the benzene rings lying approximately parallel to the *ab* plane and separated by *c*/2, giving pseudo *C* centering (Fig. 2). However, the 3,5-chlorine substituents do not superimpose, this effect being less pronounced than is observed in 2,5-D where exact superimposition occurs.

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[3-Benzyl-5-(4-nitrophenyl)-2-phenyl-1,3-thiazolio]-4-oxide

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Abstract. $C_{22}H_{16}N_2O_3S$, orthorhombic, *Pbca*, $a = 14{\cdot}77$ (2), $b = 7{\cdot}94$ (1), $c = 32{\cdot}76$ (2) Å, $Z = 8$, $D_c = 1{\cdot}34$ g cm^{-3}, μ(Mo $K\alpha$) = $1{\cdot}96$ cm^{-1}. The structure was refined to an *R* value of 0·11 for 592 independent reflexions. The mesoionic character of the molecule is established.

Introduction. The mesoionic character of the molecule is of interest and it was decided to determine its geometry by X-ray diffraction. Crystals of the title compound were grown by slow evaporation from a saturated solution of ethanol. The space group was determined from Weissenberg photographs. Cell constants were obtained by a least-squares analysis of the settings of 42 reflexions. Three-dimensional intensity data were collected on an Enraf–Nonius automated three-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation and the $\theta/2\theta$ scan mode (scan range = 1·0°). 1024 reflexions were first included in the calculations. Lorentz and polarization corrections were applied, but the absorption effect was ignored.

The overall temperature factor (3·0 Å^2) was calculated by adjusting the centrosymmetric experimental statistics to the theoretical ones (Délugeard, Toupet & Messager, 1978) (there is no ambiguity in the space group). The structure was solved by a modified version of the *MULTAN* direct phase determination procedure (Germain, Main & Woolfson, 1971; Declercq, Germain, Main & Woolfson, 1973). The convergence elimination algorithm was performed on a set of 160 reflexions with $|E| > 1{\cdot}38$. An E map computed with the phases of the second most reliable set (COMBINED FOM = 2·2636) showed clearly 24 of the 28 non-hydrogen atoms of the molecule. Fourier calculations revealed the four remaining atoms. The structure was refined by the least-squares method (Busing, Martin & Levy, 1962). Because of the poor quality of the crystal, only 592 reflexions [$I > 2\sigma(I)$] were used during this refinement, and owing to the low value of the reflexion-to-parameter ratio, arising from the paucity of data, refinement of anisotropic thermal parameters was not attempted. The final agreement value was $R = 0{\cdot}11$. The atomic scattering factors were those given in *International Tables for X-ray Crystallography* (1974). The final atomic coordinates and thermal parameters are given in Table 1.*

Table 1. *Final positional* (×10^4) *and thermal parameters with standard deviations in parentheses*

	x	y	z	B (Å^2)
C(1)	2484 (15)	10570 (30)	1412 (5)	2·0 (4)
C(2)	2650 (13)	9715 (30)	1045 (5)	1·5 (5)
C(3)	1005 (14)	9880 (30)	1228 (6)	2·6 (5)
C(4)	3484 (14)	9331 (29)	856 (6)	2·4 (5)
C(5)	4313 (15)	9949 (33)	1032 (7)	3·4 (6)
C(6)	5131 (15)	9612 (31)	833 (7)	3·2 (5)
C(7)	5108 (14)	8575 (32)	481 (6)	2·5 (5)
C(8)	4326 (17)	7962 (36)	288 (7)	4·3 (6)
C(9)	3489 (16)	8356 (31)	474 (6)	3·2 (6)
C(10)	4 (15)	9810 (31)	1226 (6)	2·8 (5)
C(11)	−515 (18)	9769 (36)	1592 (8)	5·3 (7)
C(12)	−1502 (20)	9546 (38)	1566 (9)	6·5 (8)
C(13)	−1895 (16)	9437 (37)	1186 (8)	5·1 (7)
C(14)	−1369 (15)	9400 (32)	831 (7)	3·7 (6)
C(15)	−441 (16)	9538 (34)	847 (8)	4·4 (6)
C(16)	1225 (14)	11819 (32)	1843 (7)	3·2 (6)
C(17)	1179 (14)	10789 (35)	2243 (7)	3·0 (5)
C(18)	1607 (16)	9277 (34)	2305 (7)	3·5 (5)
C(19)	1604 (19)	8381 (35)	2683 (9)	5·4 (6)
C(20)	1132 (19)	9129 (42)	3004 (9)	5·6 (7)
C(21)	678 (21)	10725 (46)	2964 (10)	7·0 (8)
C(22)	702 (18)	11611 (38)	2574 (9)	5·9 (8)
S	1605 (4)	9024 (9)	847 (2)	2·9 (1)
N(1)	1523 (11)	10709 (23)	1502 (5)	2·6 (4)
N(2)	5975 (16)	8308 (33)	275 (7)	5·7 (6)
O(1)	3025 (9)	11288 (20)	1650 (4)	3·1 (4)
O(2)	6658 (14)	8879 (27)	414 (5)	6·5 (5)
O(3)	5975 (13)	7303 (29)	−4 (6)	6·5 (5)

Table 2. *Bond distances* (Å) *with standard deviations in parentheses*

C(1)–C(2)	1·40 (3)	C(3)–C(10)	1·48 (3)
C(2)–C(4)	1·41 (3)	C(10)–C(11)	1·42 (3)
C(4)–C(5)	1·44 (3)	C(11)–C(12)	1·47 (4)
C(5)–C(6)	1·40 (3)	C(12)–C(13)	1·38 (4)
C(6)–C(7)	1·42 (3)	C(13)–C(14)	1·40 (3)
C(7)–N(2)	1·46 (3)	C(14)–C(15)	1·38 (3)
O(2)–N(2)	1·20 (3)	C(15)–C(10)	1·42 (3)
O(3)–N(2)	1·21 (3)	N(1)–C(16)	1·49 (3)
C(7)–C(8)	1·40 (3)	C(16)–C(17)	1·55 (3)
C(8)–C(9)	1·41 (3)	C(17)–C(18)	1·37 (4)
C(4)–C(9)	1·47 (3)	C(18)–C(19)	1·43 (4)
S–C(2)	1·76 (2)	C(19)–C(20)	1·39 (4)
S–C(3)	1·67 (2)	C(20)–C(21)	1·44 (5)
O(1)–C(1)	1·25 (2)	C(21)–C(22)	1·46 (4)
N(1)–C(1)	1·45 (3)	C(22)–C(17)	1·45 (4)
N(1)–C(3)	1·35 (3)		

Table 3. *Bond angles* (°) *with standard deviations in parentheses*

S–C(2)–C(1)	108 (1)	C(8)–C(7)–N(2)	118 (2)
S–C(3)–N(1)	113 (2)	C(7)–N(2)–O(2)	121 (2)
S–C(3)–C(10)	121 (2)	C(7)–N(2)–O(3)	116 (2)
S–C(2)–C(4)	122 (1)	O(2)–N(2)–O(3)	122 (2)
C(2)–S–C(3)	94 (1)	C(3)–C(10)–C(11)	122 (2)
C(1)–C(2)–C(4)	129 (2)	C(3)–C(10)–C(15)	118 (2)
C(2)–C(1)–N(1)	112 (2)	C(11)–C(10)–C(15)	119 (2)
C(2)–C(1)–O(1)	130 (2)	C(10)–C(11)–C(12)	119 (2)
O(1)–C(1)–N(1)	117 (2)	C(11)–C(12)–C(13)	119 (2)
C(1)–N(1)–C(3)	112 (2)	C(12)–C(13)–C(14)	121 (2)
C(1)–N(1)–C(16)	119 (2)	C(13)–C(14)–C(15)	121 (2)
C(3)–N(1)–C(16)	128 (2)	C(14)–C(15)–C(10)	120 (2)
N(1)–C(3)–C(10)	126 (2)	N(1)–C(16)–C(17)	110 (2)
C(2)–C(4)–C(5)	120 (2)	C(16)–C(17)–C(18)	125 (2)
C(2)–C(4)–C(9)	119 (2)	C(16)–C(17)–C(22)	115 (2)
C(5)–C(4)–C(9)	121 (2)	C(18)–C(17)–C(22)	121 (2)
C(4)–C(5)–C(6)	119 (2)	C(17)–C(18)–C(19)	124 (2)
C(5)–C(6)–C(7)	118 (2)	C(18)–C(19)–C(20)	116 (3)
C(6)–C(7)–C(8)	126 (2)	C(19)–C(20)–C(21)	123 (3)
C(7)–C(8)–C(9)	117 (2)	C(20)–C(21)–C(22)	120 (3)
C(8)–C(9)–C(4)	119 (2)	C(21)–C(22)–C(17)	117 (3)
C(6)–C(7)–N(2)	116 (2)		

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33584 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Equations of least-squares planes and distances* (Å) *of atoms from them*

The equations are of the form $AX + BY + CZ = D$, where X, Y and Z are the coordinates (in Å) referred to the orthogonal axes a, b, and c respectively and D is the origin-to-plane distance.

Plane I: S, N(1), C(1), C(2), C(3)

$0{\cdot}0731X - 0{\cdot}8489Y + 0{\cdot}5234Z + 4{\cdot}4575 = 0$

C(1)	−0·0214	C(4)	−0·0125
C(2)	0·0129	C(10)	0·0529
C(3)	−0·0117	C(16)	0·2165
S	−0·0009	O(1)	−0·0053
N(1)	0·0210		

Plane II: benzene ring [C(4) to C(9)]

$0{\cdot}0747X - 0{\cdot}8351Y + 0{\cdot}5449Z + 4{\cdot}2891 = 0$

C(4)	−0·0151	C(2)	−0·0052
C(5)	−0·0102	C(3)	−0·0404
C(6)	0·0304	C(10)	0·0275
C(7)	−0·0248	S	0·0051
C(8)	−0·0019	N(1)	0·0374
C(9)	0·0216	N(2)	0·0691

Plane III: benzene ring [C(10) to C(15)]

$0{\cdot}1007X - 0{\cdot}9926Y + 0{\cdot}0676Z + 7{\cdot}4273 = 0$

C(10)	0·0323	C(3)	−0·0620
C(11)	−0·0037		
C(12)	−0·0271		
C(13)	0·0294		
C(14)	0·0009		
C(15)	−0·0318		

Plane IV: benzene ring [C(17) to C(22)]

$0{\cdot}8358X + 0{\cdot}4745Y + 0{\cdot}2764Z - 7{\cdot}5619 = 0$

C(17)	0·0102	C(16)	−0·0717
C(18)	−0·0034		
C(19)	−0·0048		
C(20)	0·0056		
C(21)	0·0014		
C(22)	−0·0090		

Plane V: C(7), N(2), O(2), O(3)

$0{\cdot}1422X - 0{\cdot}7800Y + 0{\cdot}6094Z + 3{\cdot}2917 = 0$

C(7)	−0·0138
N(2)	0·0487
O(2)	−0·0180
O(3)	−0·0169

Dihedral angles (°)

Planes	I	II	III	IV
V	7·46	6·21	33·92	85·25
IV	78·63	79·44	68·40	
III	27·70	29·15		
II	1·48			

Discussion. Fig. 1 shows a projection of the molecule onto the XZ plane of the cell. Bond lengths and angles are given in Tables 2 and 3. The equations of some least-squares planes with the displacements of relevant atoms from them are listed in Table 4. There is some dispersion in the values of the bond lengths and angles, particularly in the benzene rings where the distances vary from 1·37 to 1·47 Å and the angles from 116 to 126°. This discrepancy can be explained by the poor quality of the crystal (all attempts to obtain larger crystals failed), and the mediocre measurement of the weak reflexions. Under these conditions we have considered it useless to introduce the H atoms in the refinement. Some intermolecular distances <3·60 Å are given in Table 5; the shortest is 3·10 Å between O(3) at x,y,z and S at $\frac{1}{2} + x, \frac{3}{2} - y, -z$.

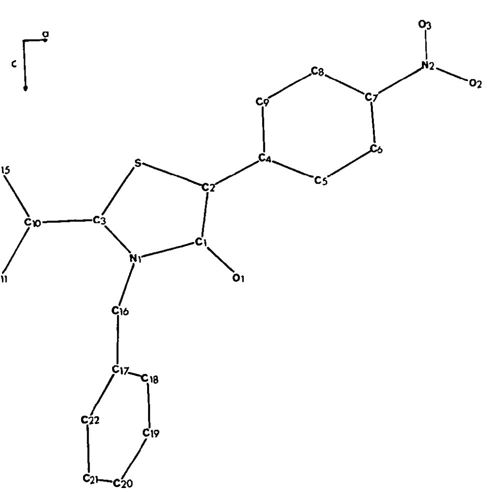

Fig. 1. A projection of the molecule onto the plane XZ showing the atom-numbering scheme.

Table 5. *Selected intermolecular distances* <3·60 Å

Symmetry code

(*a*)	$\frac{1}{2}+x$,	$\frac{3}{2}-y$,	$-z$	(*c*)	$1-x$,	$2-y$,	$-z$
(*b*)	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	z	(*d*)	$-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$

O(3)–S^a	3·10	C(8)–N(2)^c	3·52
O(1)–C(18)^b	3·24	C(21)–C(11)^d	3·53
O(1)–S^b	3·45	C(5)–S^b	3·56
C(15)–C(7)^b	3·46	O(1)–C(1)^b	3·57
O(1)–C(3)^b	3·48	N(1)–C(4)^b	3·57
C(1)–C(2)^b	3·51	C(1)–S^b	3·57
O(1)–C(2)^b	3·51		

In conclusion, this work shows the general molecular geometry, establishing unambiguously the mesoionic character (Baudy & Robert, 1976).

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