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The Crystal and Molecular Structure of *N*-(1,2,3,5-Tetramethyl-4-pyrazolio)toluene-*p*-sulphonamidate, $C_{14}H_{19}N_3O_2S$, a Mesoionic Pyrazole

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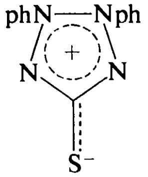
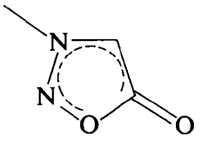
The structure of *N*-(1,2,3,5-tetramethyl-4-pyrazolio)toluene-*p*-sulphonamidate has been determined from 2383 significant independent reflexions collected on an automated four-circle diffractometer. The crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions $a = 8{\cdot}295$ (2), $b = 13{\cdot}353$ (3), $c = 13{\cdot}759$ (3) Å, $\beta = 105{\cdot}90$ (1)°. The structure has been refined by a least-squares method to give an R value of 0·051. The bond lengths in the pyrazole moiety indicate extensive electron delocalization over the whole ring. The exocyclic C–N and N–S distances are 1·396 (3) and 1·558 (2) Å respectively. The data are consistent with a dipolar structure containing an essentially positive aromatic pyrazolium ring attached to a negatively charged N atom.

Introduction

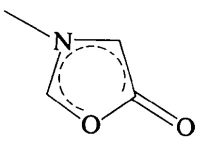
Mesoionic compounds (Ollis & Ramsden, 1976) containing a five-membered ring may be divided into two classes, in which the hetero-atoms contributing two π-electrons are, respectively, non-adjacent and adjacent. Many compounds in the first category are known, including the sydnones (Stewart, 1964) and the münchnones (Huisgen, 1967), and examples of new systems appear continually (Ollis, Ramsden & Hanley, 1976; Potts, Kane, Carnahan & Singh, 1975), a notable newcomer being a selenazolium-4-olate (Cava & Saris, 1975). In contrast, our knowledge of compounds in the second class is very limited. Although dehydrodithizone (2,3-diphenyltetrazolium-5-thiolate) (I) was the first mesoionic compound to be prepared (Fischer & Besthorn, 1882), the only other members of this family are the corresponding tetrazolium-5-olate (Bamberger, 1911) and 4-*N*-benzoylamidate (Bamberger, Padova & Ormerod, 1926), pyrazolium-4-olates (Nye & Tang, 1972; Nye, O'Hare & Tang, 1973, and references cited therein), pyrazolium-4-sulphonylamidates (Boyd & Norris, 1974), 3,5-diphenyl-1,2-dithiolium-4-olate (Schönberg & Frese, 1970), 2,3-dimethylisothiazolium-4-*p*-toluenesulphonylamidate (Boyd & Norris, 1974), and an unstable isoxazolium-4-*p*-toluenesulphonylamidate, which was only obtained in solution (Boyd & Norris, 1974). X-ray structures of several derivatives of sydnones (Bärnighausen, Jellinek, Munnik & Vos, 1963; Hope & Thiessen, 1969) and of a münchnone (Boyd, Davies, Donaldson, Silver & Wright, 1975) have been published and it appears that these compounds are best represented by formulae, such as (II) and (III), in which the π-conjugation does not extend over the whole ring, so that they cannot be regarded as aromatic. Of compounds in the second class, only dehydrodithizone has been submitted to X-ray analysis (Kuski & Fernando, 1970). The crystal structure was found to consist of infinite chains of alternating tetrazole rings and S atoms, each S atom be-



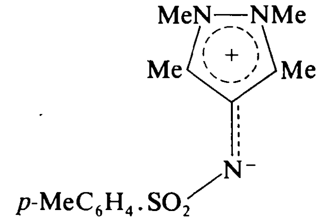
(I)



(II)



(III)



(IV)

ing sandwiched between planes of tetrazole rings above and below. The bond lengths within the ring and the C—S distance, which is intermediate between a double and a single bond, are consistent with considerable charge separation, as expressed by formula (I).

We now report the structure of the title compound (IV), another member of the dehydrothizone class.

Experimental

N-(1,2,3,5-Tetramethyl-4-pyrazolio)toluene-*p*-sulphonamidate (Boyd & Norris, 1974) forms colourless prismatic crystals. An approximately equi-dimensional crystal fragment, maximum dimension 0·2 mm, was mounted about the *a* axis, coated with shellac to prevent deliquescence and used in the X-ray analysis. Intensity data were collected on a Hilger & Watts Y290 automated four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation and the $\omega/2\theta$ scan mode. Gradual variations in the experimental conditions were monitored by measuring three reference reflexions after every 50 reflexions. The overall variation in the sum of the reference-reflexion intensities was 3·9% and the reference sums were used to scale the observed intensities by interpolation between groups of reference reflexions.

3672 reflexions were measured over the range $0° \leq \theta \leq 70°$. Averaging of the symmetry-related reflexions (562 reflexions with an agreement residual of 0·023) yielded 2731 reflexions of which 2383 had $I \geq 3\sigma(I)$ and were thereby classified as significant. The data were corrected for Lorentz and polarization effects but not for absorption: $\mu(\mathrm{Cu}\ K\alpha) = 19{\cdot}58\ \mathrm{cm}^{-1}$.

Crystal data

$C_{14}H_{19}N_3O_2S$, $M_r = 293{\cdot}4$. Monoclinic, $a = 8{\cdot}295\,(2)$, $b = 13{\cdot}353\,(3)$, $c = 13{\cdot}759\,(3)$ Å, $\beta = 105{\cdot}90\,(1)°$, $D_m = 1{\cdot}321$ g cm^{-3} (by flotation in a mixture of chloroform and ethanol), $Z = 4$, $D_c = 1{\cdot}329$ g cm^{-3}, $F(000) = 668$. The conditions limiting possible reflexion, $0k0$, $k = 2n$ and $h0l$, $l = 2n$, uniquely determine the space group as $P2_1/c$ (C_{2h}^5, No. 14).

Structure solution and refinement

The S atom was located from a three-dimensional Patterson synthesis and the remaining non-hydrogen atoms were then obtained by the iterative Fourier synthesis technique to give an R value of 0·238.

The structure was refined by a full-matrix least-squares technique using only the significant reflexions. After initial isotropic refinement a difference Fourier synthesis revealed the phenyl H atoms but showed only diffuse electron density maxima in the vicinity of the methyl groups. In subsequent calculations, the H atoms were placed in calculated positions with a C—H bond length of 1·0 Å assumed and no attempt was made to refine the atomic parameters of these atoms. For the methyl groups a tetrahedral geometry was assumed with one H atom constrained to lie in the plane of the pyrazole ring.

Further refinement was carried out with all non-hydrogen atoms treated anisotropically until all the parameter shifts were less than the corresponding estimated standard deviations. The final values of R and R' [$= (\Sigma\, w\Delta^2/\Sigma F_o^2)^{1/2}$] were 0·051 and 0·071 respectively. Throughout the refinement, weights were assigned to the unscaled observed structure factors according to the function $w = a_0$ for $F_o \leq 30{\cdot}0$ otherwise $w = [1 - \exp(-a_1 \sin^2\theta/\lambda^2)]/(a_2 + |F_o| + a_3|F_o|^2)$;

Table 1. *Fractional atomic coordinates* (× 10^4)

Estimated standard deviations are given in parentheses. All hydrogen atoms were assigned an isotropic thermal parameter, $U = 0{\cdot}10$ Å^2; the expression used was $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$.

	x	*y*	*z*
S	7840·2 (7)	179·0 (5)	2085·2 (4)
O(1)	7629 (2)	−267 (1)	1099 (1)
O(2)	6681 (3)	−151 (2)	2634 (2)
N(1)	7935 (3)	1335 (2)	1960 (2)
N(2)	8760 (3)	2934 (2)	4123 (2)
N(3)	7059 (3)	2914 (2)	3852 (2)
C(1)	9840 (3)	−242 (2)	2821 (2)
C(2)	11209 (3)	−160 (2)	2426 (2)
C(3)	12785 (3)	−456 (2)	2985 (2)
C(4)	13033 (3)	−838 (2)	3952 (2)
C(5)	11670 (4)	−893 (2)	4354 (2)
C(6)	10082 (4)	−602 (2)	3794 (2)
C(7)	14752 (4)	−1193 (3)	4544 (3)
C(8)	7928 (3)	1925 (2)	2796 (2)
C(9)	9307 (3)	2341 (2)	3492 (2)
C(10)	6524 (3)	2314 (2)	3041 (2)
C(11)	11121 (3)	2211 (2)	3575 (3)
C(12)	9736 (4)	3464 (2)	5018 (2)
C(13)	6089 (4)	3567 (3)	4336 (2)
C(14)	4720 (3)	2145 (2)	2529 (2)
H(2)	11050	115	1730
H(3)	13757	−395	2691
H(5)	11838	−1147	5058
H(6)	9113	−653	4093
H(71)	15562	−1092	4131
H(72)	15132	−800	5185
H(73)	14701	−1920	4706
H(111)	11266	1706	2996
H(112)	11663	2924	3484
H(113)	11745	1907	4305
H(121)	11050	3378	5083
H(122)	9415	4246	4953
H(123)	9463	3160	5679
H(131)	6923	3940	4970
H(132)	5431	4115	3801
H(133)	5202	3126	4593
H(141)	3969	2558	2914
H(142)	4447	2394	1758
H(143)	4440	1360	2544

values of $a_0 = 0{\cdot}01$, $a_1 = 20{\cdot}0$, $a_2 = 20{\cdot}0$ and $a_3 = 0{\cdot}002$ were used in the final cycle. An analysis of this weighting scheme in terms of batches of increasing $\sin\theta/\lambda$ and $|F_o|$ showed a constancy in the values of $\Sigma\, w\Delta^2/n$. A final difference Fourier synthesis confirmed the correctness of the refinement.

Throughout the structure-factor calculations the atomic scattering factors listed by Hanson, Herman, Lea & Skillman (1964) were used. All computations were performed on the CDC6600 computer at the University of London Computer Centre.

The final atomic coordinates are given in Table 1.*

Discussion

Fig. 1 is a stereodrawing of the molecule viewed perpendicular to the plane defined by the atoms O(1), C(6) and C(10). Fig. 2 is a schematic drawing of the molecule showing the atomic labelling and the intramolecular bond lengths and angles, together with their estimated standard deviations. Further details of the molecular geometry are given in Table 2.

The pyrazole ring is planar within experimental error. The methyl C atoms, C(11) and C(14), attached to the pyrazole ring C atoms, C(9) and C(10) respectively, lie nearly in this plane, but the methyl C atoms, C(12) and C(13), attached to N(2) and N(3) are displaced either side of the plane by 0·097 and −0·131 Å respectively; N(1) is displaced out of the plane of the pyrazole ring by −0·107 Å. The C—C bond lengths, average value 1·394 (3) Å, the C—N bond lengths, average value 1·344 (3) Å, and the N—N bond length, 1·358 (3) Å, in the pyrazole ring are similar to those observed for pyrazole itself (LaCour & Rasmussen, 1973) and indicate a high degree of delocalized π-bonding. The N—methyl bond lengths, average value 1·462 (3) Å, compare to the value of 1·47 Å for a single N—C(sp^3) bond, whereas the ring C—methyl bond lengths, average value 1·487 (4) Å, are as expected for a C(sp^2)—C(sp^3) linkage.

The N(1)—C(8) bond distance, 1·396 (3) Å, is significantly shorter than the N—phenyl separation of 1·438 (3) Å in methanesulphonanilide (Klug, 1968), which is essentially a pure N—C(sp^2) single bond, and indicates some π-electron delocalization.

The S—N bond length is 1·558 (2) Å. The S—N bond length in the structures of the sulphonylamides so far determined ranges from 1·600 (9) Å in sulphamide (Trueblood & Mayer, 1956) through 1·633 (2) Å in methanesulphonanilide (Klug, 1968) and 1·633 (3) Å in *trans-N,N'* - dibenzenesulphonyl - 2,5 - dihydroxypiperazine (Karle, 1973) to 1·681 (5) Å in *trans*-4-*tert*-butyl-1-(*N*-ethyl-*N*-*p*-toluenesulphonylamino)-1-thioniacyclohexane fluoroborate (Cook, Glick, Rigau & Johnson, 1971); the value of 1·58 (1) Å in benzenesulphonamide-*p*-(tetrahydro-2*H*-1,2-thiazin-2-yl) *S,S*-dioxide (Aupers, Carlisle & Lindley, 1974) is unreliable because of the high thermal parameters of the sulphamide atoms. In these compounds the N atom lies in a distorted trigonal pyramidal environment, but in all cases the lone pair of electrons on this atom is involved in π-bonding with the S atom; *cf*. the formal N—S single bond value of 1·772 (1) Å in sulphamic acid (Cameron, Duncanson & Morris, 1976) or the value of 1·74 Å for the sum of the respective tetrahedral covalent radii (Pauling, 1960).

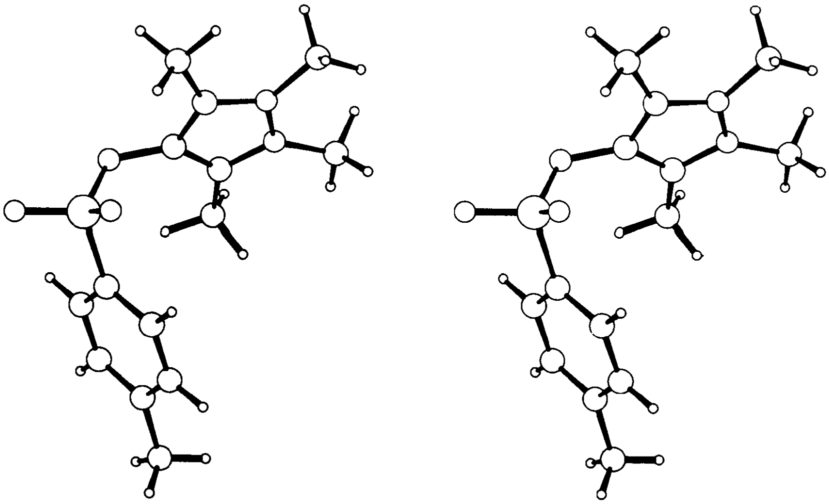


Fig. 1. Stereodrawing of the molecule viewed perpendicular to the plane defined by the atoms O(1), C(6) and C(10).

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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 32428 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

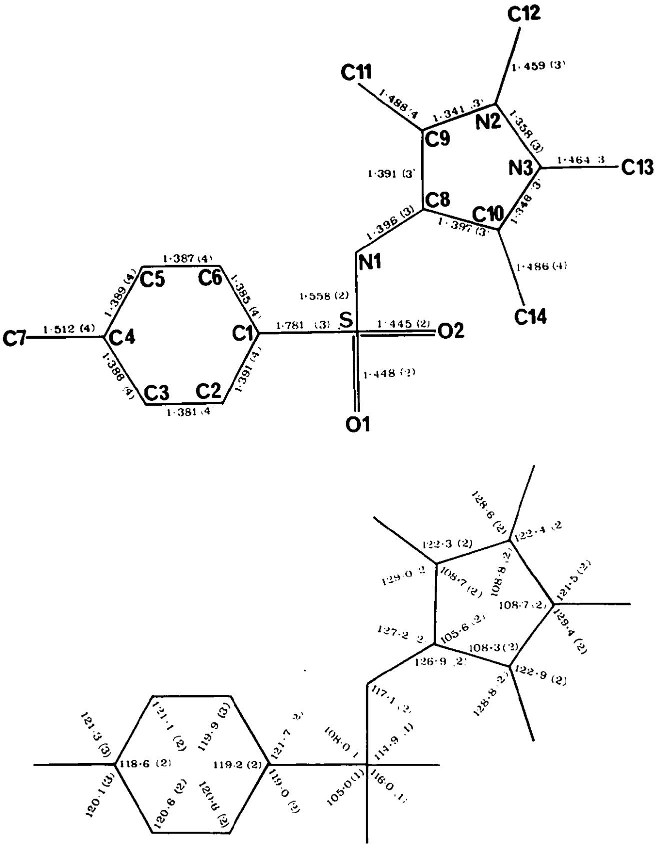

Fig. 2. Schematic drawing of the molecule showing the atomic labelling and intramolecular bond lengths and angles, together with their estimated standard deviations. Angles not shown: O(1)–S–N(1) 107·5 (1), O(2)–S–C(1) 104·9 (1)°.

In the sulphonium-stabilized ylides of the type X^+—N^-—SO_2R (where R = p-tolyl or Me), the imine–sulphonyl bond distance ranges from 1·581 (10) Å in S,S-diphenyl-N-p-tolylsulphonylsulphilimine (Kálmán, 1967) through 1·592 (2) Å in N-(trimethylammonio)toluene-p-sulphonamidate (Cameron, Duncanson & Morris, 1976) to 1·618 (7) Å in S-propyl(S-phenyl)-N-p-tolylsulphonylsulphilimine (Kálmán & Sasvári, 1972), indicating an increase in the π-bonding character of this bond. The S—N length in the present compound indicates a further increase in the π-bonding character and clearly supports the mesoionic formulation (IV).

Table 2. *Molecular geometry*

Equations of least-squares planes and distances (Å) of atoms from the planes. X, Y, and Z are orthogonal coordinates (Å) referred to axes along **a***, **b** and **c** respectively.

Plane (i)	N(2), N(3), C(8), C(9) and C(10)
	$0·0177X - 0·7774Y + 0·6287Z = -0·6053$
	N(2) −0·001, N(3) 0·005, C(8) 0·005, C(9) −0·003, C(10) −0·006, C(11) −0·029, C(12) 0·097, C(13) −0·131, C(14) −0·041, N(1) −0·107
Plane (ii)	C(1), C(2), C(3), C(4), C(5) and C(6)
	$0·1813X + 0·9263Y + 0·3303Z = 1·6772$
	C(1) −0·010, C(2) 0·006, C(3) 0·004, C(4) −0·011, C(5) 0·008, C(6) 0·003, C(7) −0·062, S 0·037
Plane (iii)	S, N(1) and C(1)
	$0·2850X - 0·1334Y - 0·9492Z = 0·7187$
	O(1) 1·274, O(2) −1·172, C(8) −1·201

Dihedral angles (°) between normals to planes

Planes	
(i) and (ii)	120·6
(i) and (iii)	119·2
(ii) and (iii)	112·7

The distorted tetrahedral configuration around the S atom is closely similar to that found in other molecules containing a —C(SO_2)N— moiety (see, for example, Karle, 1973, and references cited therein). The O—S—O angle is opened out beyond the tetrahedral angle to 116·0 (1)° giving an O(1)—O(2) separation of 2·45 Å comparable to the values of 2·42 and 2·53 Å for the N(1)—O(1) and N(1)—O(2) distances respectively.

The phenyl ring is planar and the S atom and the

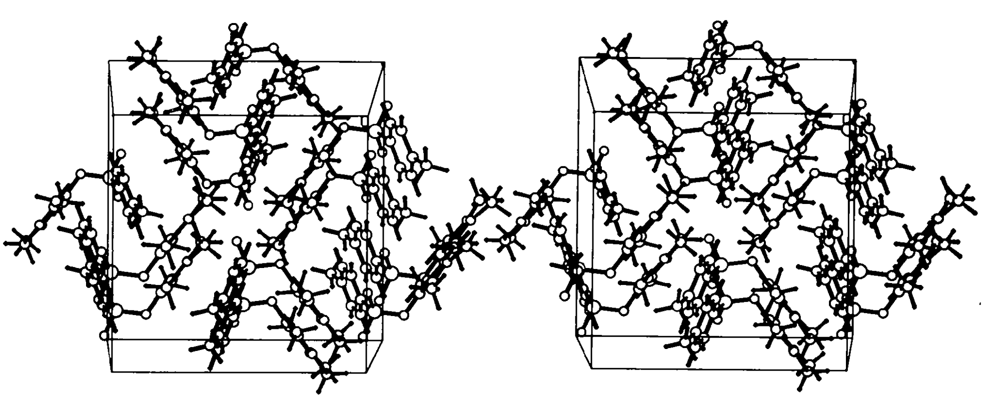

Fig. 3. Stereodrawing of the molecular packing viewed along **a**.

methyl C atom, C(7), lie approximately in the plane; the displacements are 0·037 and −0·062 Å respectively.

The magnitude of the S–phenyl distance, 1·781 (3) Å, is slightly larger than the average value of 1·75 Å found in the sulphonylamides and is probably associated with the increase in π-bonding character in the S–N(1) linkage. In the sulphonium-stabilized ylides, X^+–N^-–S, where X is not S, the S–phenyl bond lengths average 1·78 Å.

The dihedral angles between the plane defined by S, C(1) and N(1) and the planes defined by the pyrazole and phenyl rings are 119·2 and 112·7° respectively; the torsion angle C(1)–S–N(1)–C(8) is −75·1°.

The molecular packing is shown by a stereodrawing along **a** in Fig. 3. There are no intermolecular contacts significantly less than the sum of the respective van der Waals radii.

We conclude that the structure of the pyrazolium-*p*-toluenesulphonylamidate is consistent with the mesoionic formulation (IV), in which the exocyclic N atom bears a formal negative charge and the pyrazole ring a formal positive charge, and that the present compound, like dehydrodithizone, may be considered to be aromatic. Further, this formulation can be used to rationalize the mechanism of thermal isomerization of the pyrazolium-4-sulphonamidates and the Michael-type addition to dimethyl acetylenedicarboxylate (Boyd & Norris, 1974) which are believed to occur by similar reaction pathways.

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