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Acta Cryst. (1992). **C48**, 1471–1474

Mesoionic Compounds. 3.* Structure of the Hydrochloride of 5-(4-Methoxyphenyl)-4-phenyl-1,3,4-thiadiazolium-2-phenylaminide

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(Received 17 October 1991; accepted 7 January 1992)

Abstract. 5-(4-Methoxyphenyl)-4-phenyl-2-phenylamino-1,3,4-thiadiazolium chloride, $C_{21}H_{18}N_3OS \cdot Cl^-$, $M_r = 395.91$, orthorhombic, *Pbca*, $a = 15.809$ (4), $b = 12.207$ (2), $c = 19.772$ (5) Å, $V =$

3815.5 (1.4) Å³, $Z = 8$, $D_x = 1.378$ g cm⁻³, $\lambda(Mo K\alpha) = 0.7107$ Å, $\mu = 3.2$ cm⁻¹, $F(000) = 1648$, $T = 297$ K, $R = 0.041$ for 1159 reflections with $|F_o| > 2\sigma(|F_o|)$. The pentatomic ring has two conjugated systems separated by S—C and N—N single bonds.

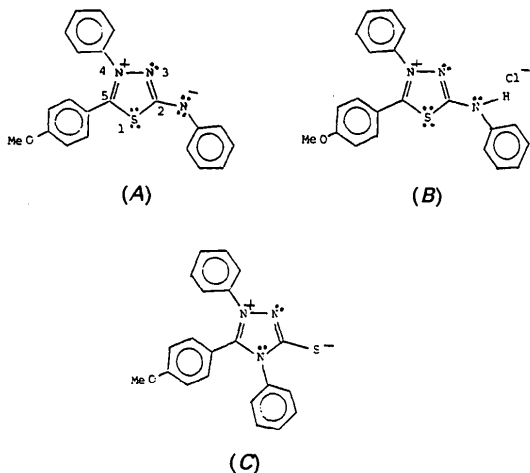
* Part 2: Cheung, Galembeck, Miller, de Oliveira, Pereira & Simas (1992).

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Introduction. The concept of mesoionic compounds has developed gradually, undergoing a number of

changes over the years. A description of mesoionic compounds which corresponds to current thinking is that they are a class of heterocyclic betaines, characterized by possessing a pentatomic heterocyclic system associated with a sextet of p and π electrons, and also supporting a positive charge. This is counter-balanced by formal negative charge on the α atom of a side chain. It must be stressed that the extent of delocalization of the p and π electrons and of positive and negative charges within, and indeed outside, the pentatomic heterocycle has not yet been sufficiently treated and clarified. This applies also to the degree of aromaticity and of stabilization energy. Furthermore, it should be expected that these may vary from system to system. Mesoionic compounds are also characterized by a substantial separation of charge for which there is ample direct and indirect evidence through determination of dipole moments (e.g., Earl, Leake & Le Fèvre, 1948) or as a result of kinetic studies (Echevarria & Miller, 1989).

4-Phenyl-5-(4-methoxyphenyl)-1,3,4-thiadiazolium-2-phenylaminide (*A*) and its hydrochloride (*B*), the X-ray diffraction study of which is reported in the present work, are best represented as shown below, following chemical and spectroscopic evidence.



The evidence allows one to suggest that in (*A*) and in (*B*) the positive charge is substantially associated with the N(4) atom (and its attached phenyl group), whereas the negative charge, formally on the exocyclic N atom, is substantially delocalized to its attached phenyl group and to the N(3) atom: less so, but still significant in the hydrochloride (*B*).

A further point of great importance is that the mesoionic compound (*A*) rearranges to its isomer (*C*), also considered mesoionic, which is more stable, viz., 1,4-diphenyl-5-(4-methoxyphenyl)-1,3,4-triazolium-2-thiolate. In the rearrangement, the exocyclic

N atom of (*A*) becomes N(1) of (*C*), while the S(1) atom of (*A*) becomes the exocyclic S atom of (*C*).

One can thus infer from this collection of evidence that in compounds (*A*) and (*B*):

(a) the N(3) to N(4) bond and the S(1) to C(2) bond are close to single bonds and that the S(1) to C(5) bond is likely to be little different from the S(1) to C(2) bond;

(b) the C(2) to exocyclic-N bond has substantial double-bond character – probably more so in the free base (*A*) than in the hydrochloride (*B*);

(c) the C(5) to N(4) bond and C(2) to N(3) bond have substantial double-bond character;

(d) N(4) has substantial positive charge, while N(3) has substantial negative charge.

Preliminary results of theoretical calculations are in accord with the inferences from chemical and spectroscopic evidence.

Experimental. A crystal of dimensions 0.09 × 0.11 × 0.25 mm was mounted on an Enraf-Nonius CAD-4 diffractometer, equipped with graphite-monochromated Mo $K\alpha$ radiation and scintillation counter. Cell parameters were determined by least squares from setting angles of 25 reflections ($9 < 2\theta < 13^\circ$) measured on the diffractometer. The intensities of 9771 reflections ($2\theta_{\max} = 44^\circ$), in the range $-16 \leq h \leq 16$, $0 \leq k \leq 12$, $-20 \leq l \leq 20$, were measured using ω - 2θ scan, ω -scan angle $(0.60 + 0.344\tan\theta)^\circ$ at 0.66 – $5.49^\circ \text{ min}^{-1}$, extended 25% on each side for background measurement. Three standard reflections measured every 4 h showed no decay. Systematic absences indicated space group $Pbca$ and this was confirmed in the structure solution. The intensity data were corrected for Lorentz and polarization effects. Averaging of equivalent reflections gave 2668 independent reflections, of which 1159 with $I > 1.5\sigma(I)$, where $\sigma^2(I) = S + 4(B1 + B2)$ (S = scan, $B1$ and $B2$ = background counts), were considered observed. $R_{\text{int}} = 0.045$ for observed reflections and 0.046 for all reflections. The structure was solved by direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and refined by full-matrix least squares with ionic

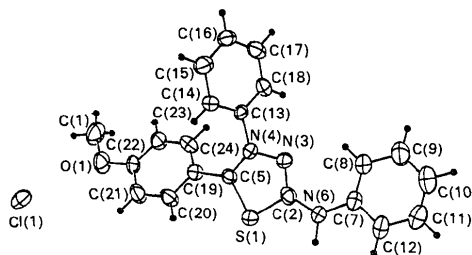


Fig. 1. ORTEPII (Johnson, 1976) drawing of the molecule with atomic numbering scheme.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2) with *e.s.d.*'s in parentheses
$$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}
Cl(1)	0.45537 (8)	0.22182 (9)	0.04311 (6)	4.82 (3)
S(1)	0.12036 (7)	0.01564 (8)	0.50847 (5)	3.22 (2)
O(1)	0.3076 (2)	0.2852 (2)	0.2571 (1)	4.76 (8)
N(3)	0.1139 (2)	0.1500 (2)	0.6103 (2)	3.16 (8)
N(4)	0.1473 (2)	0.2031 (2)	0.5539 (2)	2.66 (8)
N(6)	0.0654 (2)	-0.0282 (3)	0.6349 (2)	3.42 (9)
C(1)	0.3765 (5)	0.3605 (3)	0.2576 (2)	5.6 (1)
C(2)	0.0969 (3)	0.0486 (3)	0.5932 (2)	3.0 (1)
C(5)	0.1566 (3)	0.1467 (3)	0.4979 (2)	2.67 (9)
C(7)	0.0582 (3)	-0.0230 (3)	0.7054 (2)	3.2 (1)
C(8)	0.0914 (3)	0.0592 (3)	0.7453 (2)	4.3 (1)
C(9)	0.0830 (3)	0.0533 (4)	0.8152 (2)	5.4 (1)
C(10)	0.0410 (3)	-0.0339 (4)	0.8447 (2)	5.3 (1)
C(11)	0.0088 (3)	-0.1168 (4)	0.8044 (2)	4.9 (1)
C(12)	0.0175 (3)	-0.1123 (3)	0.7352 (2)	4.1 (1)
C(13)	0.1615 (3)	0.3199 (3)	0.5647 (2)	2.56 (9)
C(14)	0.1220 (3)	0.3929 (3)	0.5212 (2)	3.1 (1)
C(15)	0.1308 (3)	0.5044 (3)	0.5348 (2)	3.8 (1)
C(16)	0.1775 (3)	0.5393 (3)	0.5903 (2)	3.6 (1)
C(17)	0.2164 (3)	0.4642 (3)	0.6317 (2)	3.6 (1)
C(18)	0.2093 (3)	0.3530 (3)	0.6189 (2)	3.2 (1)
C(19)	0.1971 (2)	0.1841 (3)	0.4358 (2)	2.7 (1)
C(20)	0.1670 (3)	0.1495 (3)	0.3729 (2)	3.6 (1)
C(21)	0.2061 (3)	0.1840 (4)	0.3145 (2)	3.9 (1)
C(22)	0.2754 (2)	0.2530 (3)	0.3179 (2)	3.2 (1)
C(23)	0.3080 (3)	0.2845 (3)	0.3792 (2)	3.4 (1)
C(24)	0.2684 (2)	0.2511 (3)	0.4376 (2)	3.4 (1)

and atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) using the *SDP* programs (Enraf-Nonius, 1985) on a MicroVAX II computer. The H atom bonded to N(6) was located in a difference Fourier synthesis and all the other H atoms, in calculated positions, were not refined. Convergence for 244 variables by least squares with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma(F_o) = [\sigma^2(I) + (0.028F_o^2)^2]^{1/2}$ and with reflections with $F_o^2 < 0.9\sigma(F_o^2)$ being omitted, was reached at $R = 0.041$, $wR = 0.027$ and $S = 0.0769$ for 1159 reflections with $|F_o| > 2\sigma(F_o)$. $(\Delta/\sigma)_{max} = 0.01$. A final difference Fourier map was featureless with maximum positive and negative peaks of 0.25 and 0.20 e \AA^{-3} , respectively.

Discussion. An *ORTEPII* drawing (Johnson, 1976) of the molecule with atomic numbering scheme is shown in Fig. 1. The atomic parameters of the C, N, O and S atoms and Cl⁻ ion are listed in Table 1.* Bond lengths and bond angles and selected torsion angles are given in Table 2. The pentatomic heterocyclic ring is planar and the maximum deviation of its atoms from the least-squares plane is $0.011 (4) \text{ \AA}$. The deviation of the exocyclic N(6) atom from the

* Lists of bond distances and angles involving H atoms, torsion angles, least-squares planes, structure factors, anisotropic thermal parameters, root-mean-square amplitudes of thermal vibrations and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55016 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU0407]

Table 2. Bond lengths (\AA), angles ($^\circ$) and selected torsion angles ($^\circ$) with *e.s.d.*'s in parentheses

S(1)—C(2)	1.764 (5)	C(10)—C(11)	1.385 (6)
S(1)—C(5)	1.713 (4)	C(11)—C(12)	1.376 (6)
O(1)—C(1)	1.425 (5)	C(13)—C(14)	1.386 (5)
O(1)—C(22)	1.364 (5)	C(13)—C(18)	1.372 (5)
N(3)—N(4)	1.393 (4)	C(14)—C(15)	1.394 (5)
N(3)—C(2)	1.310 (5)	C(15)—C(16)	1.390 (6)
N(4)—C(5)	1.312 (5)	C(16)—C(17)	1.375 (6)
N(4)—C(13)	1.459 (5)	C(17)—C(18)	1.386 (6)
N(6)—C(2)	1.344 (6)	C(19)—C(20)	1.397 (6)
N(6)—C(7)	1.402 (5)	C(19)—C(24)	1.394 (5)
C(5)—C(19)	1.457 (5)	C(20)—C(21)	1.377 (6)
C(7)—C(8)	1.380 (6)	C(21)—C(22)	1.383 (6)
C(7)—C(12)	1.396 (6)	C(22)—C(23)	1.373 (6)
C(8)—C(9)	1.389 (6)	C(23)—C(24)	1.375 (6)
C(9)—C(10)	1.384 (7)		
C(2)—S(1)—C(5)	88.4 (2)	C(7)—C(12)—C(11)	119.8 (4)
C(1)—O(1)—C(22)	117.8 (3)	N(4)—C(13)—C(14)	117.9 (3)
N(4)—N(3)—C(2)	108.2 (3)	N(4)—C(13)—C(18)	119.1 (3)
N(3)—N(4)—C(5)	118.3 (3)	C(14)—C(13)—C(18)	122.9 (3)
N(3)—N(4)—C(13)	113.4 (3)	C(13)—C(14)—C(15)	117.6 (3)
C(5)—N(4)—C(13)	128.2 (4)	C(14)—C(15)—C(16)	120.3 (4)
C(2)—N(6)—C(7)	127.6 (3)	C(15)—C(16)—C(17)	120.3 (4)
S(1)—C(2)—N(3)	114.6 (3)	C(16)—C(17)—C(18)	120.5 (4)
S(1)—C(2)—N(6)	120.1 (3)	C(13)—C(18)—C(17)	118.4 (4)
N(3)—C(2)—N(6)	125.3 (4)	C(5)—C(19)—C(20)	120.4 (3)
S(1)—C(5)—N(4)	110.5 (3)	C(5)—C(19)—C(24)	121.2 (3)
S(1)—C(5)—C(19)	122.8 (3)	C(20)—C(19)—C(24)	118.4 (4)
N(4)—C(5)—C(19)	126.6 (3)	C(19)—C(20)—C(21)	120.1 (4)
N(6)—C(7)—C(8)	124.9 (4)	C(20)—C(21)—C(22)	120.1 (4)
N(6)—C(7)—C(12)	115.0 (3)	O(1)—C(22)—C(23)	115.5 (3)
C(8)—C(7)—C(12)	120.1 (4)	O(1)—C(22)—C(23)	123.8 (4)
C(7)—C(8)—C(9)	119.6 (4)	C(21)—C(22)—C(23)	120.8 (4)
C(8)—C(9)—C(10)	120.4 (4)	C(22)—C(23)—C(24)	119.1 (4)
C(9)—C(10)—C(11)	119.7 (5)	C(19)—C(24)—C(23)	121.5 (4)
C(10)—C(11)—C(12)	120.4 (4)		
C(13)—N(4)—C(5)	111.1 (6)	C(7)—N(6)—C(2)—N(3)	-12.0 (7)
N(3)—N(4)—C(13)—C(14)	-122.7 (4)	S(1)—C(5)—C(19)—C(20)	39.1 (5)
N(3)—N(4)—C(13)—C(18)	54.0 (5)	S(1)—C(5)—C(19)—C(24)	-138.2 (3)
N(4)—C(5)—C(19)—C(20)	-145.4 (4)	C(7)—N(6)—C(2)—S(1)	167.0 (3)
N(4)—C(5)—C(19)—C(24)	37.3 (6)	C(5)—N(4)—C(13)—C(18)	-131.0 (4)
C(5)—N(4)—C(13)—C(14)	52.3 (5)		

plane is $-0.041 (3) \text{ \AA}$. The N(3)—N(4) bond of $1.393 (4) \text{ \AA}$ is close to the normal single-bond length of 1.40 \AA (Sutton, 1965). The C(2)—N(3) bond length of $1.310 (5) \text{ \AA}$, the C(5)—N(4) bond length of $1.312 (5) \text{ \AA}$, and the C(2)—N(6) bond length of $1.344 (6) \text{ \AA}$ all suggest that these bonds have partial double-bond character. The S(1)—C(2) bond length of $1.764 (5) \text{ \AA}$ is comparable to the C(*sp*²)—S single bond of 1.77 \AA in acetazolamide (5-acetamido-1,3,4-thiadiazole-2-sulfonamide) (Mathew & Palenik, 1974). The S(1)—C(5) bond length of $1.713 (4) \text{ \AA}$ is significantly shorter, and is comparable to the C—S bond length of 1.712 \AA in thiophenes (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The difference in the two C—S bonds suggests that this mesoionic compound has two essentially separate conjugated systems, separated by the single bonds S(1)—C(2) and N(3)—N(4). Comparable differences in the C—S bonds have been observed, *viz.* 1.761 and 1.728 \AA in a mesoionic thiadiazole derivative (Flippen, 1972), and 1.764 and 1.730 \AA in 2,5-diamino-3*H*-1,3,4-thiadiazolium chloride (Senda, Matsuoka & Maruha, 1986). The Cl⁻ ion is 2.05 \AA from the H atom attached to N(6), 3.00 \AA from N(6) and 3.21 \AA from S(1), all at $\frac{1}{2} - x, -y, -\frac{1}{2} + z$, and

these are the only non-bonded interatomic distances less than 3.3 Å.

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Acta Cryst. (1992). **C48**, 1474–1476

Structure of *p*-*tert*-Butylbishomooxalix[4]arene–*m*-Xylene (1:1) Complex

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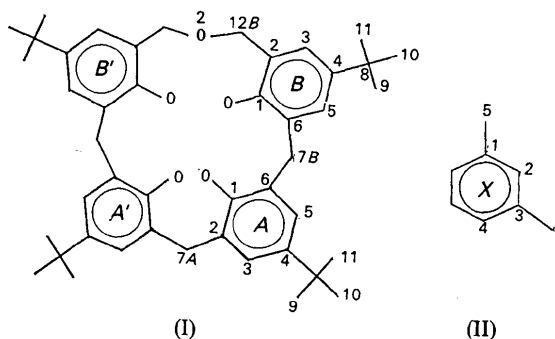
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(Received 13 September 1991; accepted 6 January 1992)

Abstract. 7,13,19,25-Tetra-*tert*-butyl-27,28,29,30-tetrahydroxy-2,3-dihomo-3-oxalix[4]arene–*m*-xylene, C₄₅H₅₈O₅.C₈H₁₀, *M_r* = 787.03, orthorhombic, *Pbcm*, *a* = 9.328 (1), *b* = 19.348 (3), *c* = 25.939 (5) Å, *V* = 4681.4 (3) Å³, *Z* = 4, *D_x* = 1.114 g cm⁻³, graphite-monochromated Cu *Kα* radiation, λ = 1.54178 Å, μ = 5.10 cm⁻¹, *F*(000) = 1704, *T* = 283 K, final *R* = 0.077 for 1446 reflections. The complex has mirror symmetry in which the plane passes through two atoms: the O and the C atoms linking the phenyl rings. CH···O, CH₃–π and CH₃–CH₃ interactions are shown to exist between the host and guest. The methyl group of the guest that penetrates into the cavity of the host shows strong CH···O interactions of 3.393 (3) and 3.617 (3) Å.

Introduction. Calixarenes (Gutsche & Muthukrishnan, 1978) are a class of synthetic macrocycles having phenolic residues in a cyclic array with methylene groups at positions *ortho* to the hydroxy group (Andreotti, Pochini & Ungaro, 1983). Some are able to form inclusion complexes with several organic guest molecules. This inclusion behaviour depends on the size of the macroring (Andreotti, Ungaro & Pochini, 1979). In order to elucidate the

particular host–guest interaction in the oxalix[4]arene, we synthesized *p*-*tert*-butylbishomooxalix[4]arene (I) and carried out an X-ray structure determination of the 1:1 complex with *m*-xylene (II).



Experimental. A colourless needle crystal (0.1 × 0.1 × 0.5 mm) suitable for X-ray data collection was mounted on a Rigaku AFC-5 diffractometer. Data were collected using ω–2θ scan technique (2θ_{max} = 126°) and graphite-monochromated Cu *Kα* radiation. Unit-cell parameters were refined based on 2θ values (48 < 2θ < 60°) of 24 reflections. A total of