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COMPARATIVE STUDY OF AROMATICITY IN FIVE-MEMBERED RINGS CONTAINING S, SO AND SO_2 GROUPS

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Owing to the importance of the concept of aromaticity, different indices have been developed to try to quantify this property. The possible π delocalization through an X—SO_n—X group (X = C, N; n = 0, 1 or 2) could explain heteroaromaticity in rings containing the moiety. For that reason, the aromaticity of five-membered sulphur-containing rings with different oxidation numbers (S, SO and SO_2) and including no (thiophene), one (isothiazole) or two (1,2,5-thiadiazole) adjacent atoms was investigated. *Ab initio* calculations were carried out to determine geometrical parameters (planarity of the ring, bond length and bond order), electronic structure (charge distribution and dipolar moment) and the participation of d-orbitals of sulphur. According to these calculations, only compounds with S(II) can be considered to be aromatic, whereas compounds bearing S(IV) or S(VI) are better described as ylides.

INTRODUCTION

Aromaticity is one of the most important concepts in organic chemistry in general, and heterocyclic chemistry in particular. This subject has been extensively investigated from a conceptual point of view.[1-3] Also, several attempts have been made to establish quantitative aromatic scales, e.g. using the concept of 'ring current',[3a] correlating classical and magnetic parameters,[4] using energetic criteria,[5] or using graph theory.[6]

So far, it has been impossible to find a unique, measurable or calculable parameter that provides a quantitative estimation of the degree of aromaticity. Nevertheless, different characteristics have been used to develop aromatic indices: from energetic criteria [resonance energy (RE),[7] resonance energy per π electron (REPE)[8,9]] to magnetic criteria (diamagnetic anisotropy,[10] proton chemical shifts and coupling constants[4]) to structural criteria (x-ray diffraction, bond orders,[3a,11,12] planarity of the ring[13]). The advantages and weaknesses of all these criteria have been extensively discussed in a fundamental paper by Katritzky *et al.*[4]

Continuing with our studies of physico-chemical properties of heterocycles containing the N—SO_2—N moiety,[14-17] here we have studied a series of five-membered sulphur-containing rings with different oxidation number (S, SO and SO_2), and including no (thiophene, **1**), one (isothiazole, **2**) or two (1,2,5-thiadiazole, **3**) adjacent N atoms (see Figure 1).

The non-aromatic behaviour observed in the chemistry of 1,2,5-thiadiazole 1,1-dioxides[18] is surprising in comparison with the non-oxidized sulphur derivatives **1**, **2** and **3**. However, there is not much information about the possible aromatic character of the *S*-oxides. Aromaticity is a very important factor in the reactivity, and also the possible biological activity, of any compound. Hence studies of effect on the aromaticity of the introduction of one or two adjacent N atoms in a sulphur-containing five-membered ring, or the variation of the oxidation state of that S atom, can help in understanding the behaviour of these compounds.

Thiophene (**1**) has been extensively investigated from the theoretical point of view using both semi-empirical and *ab initio* methods.[19] However, it continues to be the subject of a number of studies dealing with its geometry, electronic structure and aromaticity.[20] Its 1-oxide (**4**) and 1,1-dioxide (**7**) derivatives have been the subject of theoretical studies also.[19]

The structure and aromaticity of isothiazole (**2**) have been theoretically determined by different workers.[19,20b,e,f,21] In contrast, only a few 1,1-dioxide derivatives, such as saccharin, have been calculated.[19]

Different physical methods and MO calculations have been used to study the aromaticity of 1,2,5-thiadiazoles,[19] which has been found to be comparable to that of thiophene. The aromaticity of its sulphur oxide (**8**) has been the subject of interesting work.[22]

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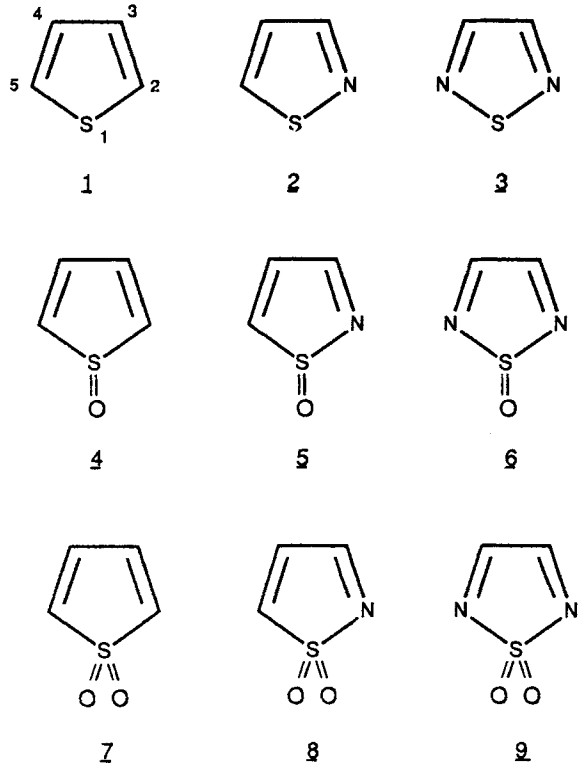

Figure 1. Structures of compounds **1**–**9**

Nevertheless, to our knowledge, no calculations on its sulphur dioxide (**9**) have been performed.

In addition, experimental data are available for the gas phase from microwave spectroscopy of thiophene and isothiazole.[18] There are also experimental data, in the solid state, obtained by x-ray spectroscopy. A search through the Cambridge Structural Database (CSD)[23] yielded 24 derivatives of thiophene (**1**) (non-fused rings), two of thiophene 1,1-dioxide (**7**), two of isothiazole (**2**), one of isothiazole 1,1-dioxide (**8**), two of 1,2,5-thiadiazole (**3**), one of its 1-oxide (**6**) and two of its 1,1-dioxide (**9**). In this paper, only some of the simplest derivatives (those with fewer and smaller non-polar substituents) will be commented upon, and their CSD code names will be used for the sake of simplicity.

As a result of all these studies, thiophene is considered to be an aromatic compound. Comparison with the other compounds in the series allows us, if not to quantify aromaticity, then at least to observe the presence or lack of certain aromatic characteristics. Further, it will be possible to observe the influence that the oxidation number of the S atom, or the substitution of an adjacent CH group by an N atom, has on the aromaticity.

From all the above indices of aromaticity, and taking into account Katritzky *et al.*'s analysis,[4] we chose parameters used successfully in previous works,[15,16] namely bond lengths, bond orders and planarity of the ring, as geometrical criteria. These indices provide a sort of 'pictorical' idea about aromaticity (levelled bond lengths and bond orders, maximum overlap of p-orbital allowed by a planar ring). However, they are not a sufficient condition for aromaticity and other criteria should also be used. For that reason, we have also analysed the electronic charge distribution and the d-orbital participation of the S atom in the π delocalization. This last point can be important with compounds with hypervalent sulphur atoms, since in these cases the electronic delocalization should take place through these d-orbitals. In the following sections, we will discuss the results obtained using geometrical criteria, the electronic structure and the participation of d-orbitals of sulphur.

COMPUTATIONAL METHODS

In order to obtain reliable results for compounds with hypervalent sulphur atoms, it is well known that the use of basis sets including polarization functions is essential.[24] Thus, large split-valence basis sets with polarization functions provide a highly accurate description of these compunds. However, a full geometry optimization with these basis sets is not economically feasible.

In previous works[15–17] we have shown that the STO-3G* basis set reproduces the geometry of compounds with hypervalent sulphur atoms reasonably well. Hence this basis set was used here to optimize compounds containing divalent and hypervalent sulphur atoms. The convergence threshold used for all the optimizations was set so that the maximum force was reduced to at least 0·000450 a.u. whereas the root-mean-square deviation of all the forces was smaller than −0·000300 a.u.

A higher accuracy is needed for a good description of properties that depend on the electronic structure (dipole moment, charge distribution, etc.). Because some of the aromaticity criteria that have been taken into account in this work rely strongly on these properties, single-point 6–31G* calculations were carried out on the fully optimized STO-3G* structures, and they are indicated as usual by 6–31G*//STO-3G*.

All the calculations at the STO-3G* level were carried out using the Gaussian 88 series of programs[25] (DEC version) and the single-point 6–31G* calculations were performed using the Gaussian 90 series of programs[26] on a Stardent/Titan 3000 workstation.

ANALYSIS USING GEOMETRICAL CRITERIA

The optimized geometrical parameters obtained for the nine compounds studied, together with some experimental microwave and x-ray spectroscopic data are

shown in Table 1. The force constants and the resulting vibrational frequencies were determined by a FREQ calculation (implemented in the Gaussian 88) on the stationary points obtained after the optimizations. All the compounds exhibited real positive and increasing frequencies as expected for true minima.

Inherent in the definition of aromaticity is the notion that a planar ring maximizes the overlap of the p-orbitals involved in the π system. Thiophene (**1**) has been found to be planar at the STO-3G* level of calculation. This is in agreement with the microwave experimental results[19] and with the geometries obtained by x-ray spectroscopy of some of its substituted derivatives,[23] as is shown in Table 1. This planar geometry is consistent with its assigned aromaticity, that is, π overlap is possible without any disruption.

Planar rings have also been obtained for **2** and **3** using the same basis set (see Table 1). This also was observed by microwave spectroscopy of **3**[19] and in the x-ray analysis of derivatives DUWFIK and HMITZC and of BIMLAK and DSPDAZ, respectively. Again, this correlates with the aromaticity previously assigned to both **2** and **3**.[19] It could seem that the substitution of the adjacent CH groups to the S atom by one or two N atoms does not affect the π delocalization and, therefore, the aromaticity.

In contrast, we obtained non-planar structures (see Table 1) for the S monoxide derivatives, which is in agreement with previous work.[19,22] The S(IV) atom presents pyramidalization and is outside the plane formed by the other four atoms by 0·196, 0·217 and 0·203 Å for **4**, **5** and **6**, respectively (see Figure 2). This fact, in principle, makes these products unlikely to be aromatic. However, if the bending is not very large

Table 1. Bond distances (Å) obtained for thiophene (**1**), isothiazole (**2**), 1,2,5-thiadiazole (**3**) and their 1-oxide (**4**), (**5**) and (**6**), and 1,1-dioxide (**7**), (**8**) and (**9**) derivatives using the STO-3G* basis set, and for some structures from the CSD[23] (X = C or N).

Compound	X_2—C_3	C_3—C_4	C_4—X_5	X_5—S_1	S_1—X_2	S=O	Planarity
1	1·349	1·436	1·349	1·693	1·693	—	Yes
Exp· **1**[a]	1·370	1·423	1·370	1·714	1·714	—	Yes
ACCTHP	1·342	1·397	1·381	1·723	1·699	—	Yes
ACETTP	1·346	1·454	1·355	1·697	1·692	—	Yes
JEDEEL	1·389	1·415	1·352	1·702	1·716	—	Yes
THIPAC	1·406	1·437	1·509	1·698	1·709	—	Yes
TPENAC	1·363	1·413	1·361	1·693	1·700	—	Yes
4	1·322	1·484	1·322	1·782	1·782	1·487	No
7	1·314	1·502	1·314	1·808	1·808	1·451 1·451	Yes
BUTSOX	1·348	1·462	1·348	1·784	1·784	1·458 1·458	Yes
MTPOFE	1·421	1·418	1·433	1·759	1·758	1·449 1·447	No
2	1·324	1·431	1·353	1·684	1·644	—	Yes
DUWFIK	1·319	1·438	1·378	1·709	1·657	—	Yes
HMITZC	1·303	1·435	1·350	1·703	1·655	—	Yes
5	1·291	1·488	1·319	1·787	1·737	1·477	No
8	1·284	1·507	1·311	1·811	1·760	1·456 1·456	Yes
BUBNOB	1·279	1·507	1·360	1·748	1·664	1·431 1·427	Yes
3	1·326	1·432	1·326	1·636	1·636	—	Yes
Exp. **3**[a]	1·327	1·417	1·327	1·630	1·630	—	Yes
BIMLAK	1·300	1·431	1·308	1·665	1·645	—	Yes
DSPDAZ	1·327	1·435	1·343	1·629	1·635	—	Yes
6	1·286	1·500	1·286	1·747	1·747	1·467	No
BESHEM	1·280	1·511	1·279	1·705	1·720	1·440	No
9	1·280	1·518	1·280	1·769	1·769	1·447 1·447	Yes
KASMOG	1·302	1·523	1·382	1·648	1·626	1·450 1·434	Yes
SACROD	1·294	1·550	1·334	1·611	1·677	1·423 1·420	Yes

[a] Experimental data for **1** and **3** obtained using microwave spectroscopy.[19]

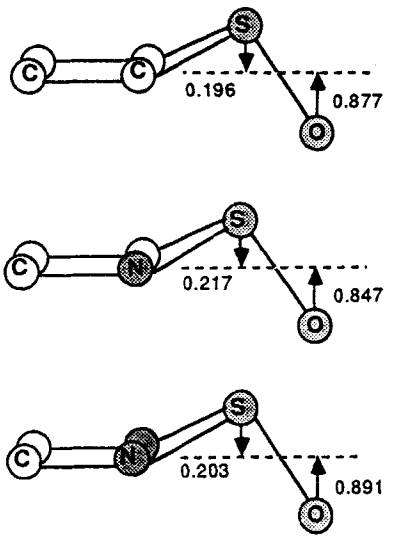

Figure 2

some π delocalization could still exist. Such delocalization has to be confirmed by other properties more related to the electronic structure.

The optimized structures of the 1,1-dioxide derivatives at the STO-3G* level were found to be planar in all cases (see Table 1, compounds **7**, **8** and **9**), except for the O atoms that were situated above and below the five-membered rings. This SO_2 group was found to lie in a plane perpendicular to that of the ring. Planarity by itself is not a sufficient reason to consider a molecule aromatic. As with the S(IV) derivatives, we have to analyse other properties to assert the possible aromaticity in these S(VI) derivatives.

The fact that the *S*-oxides are non-planar whereas the *S,S*-dioxides are planar has been observed experimentally[19,23] and theoretically[22] before. A reason for these results could be the different hybridization exhibited by the S atom in both kinds of compounds. In the 1-oxides the S atom presents a pyramidal disposition whereas the 1,1-dioxides show a tetrahedral sulphur.

Accommodating a pyramidal sulphur in a planar five-membered ring drives the O atom out of the plane and below the ring, introducing stress in the molecule. In contrast, a tetrahedral sulphur can fit in the plane of a five-membered ring without introducing any stress by orientating the O atoms, outside the ring, above and below the plane.

Without considering the nature of the other four atoms in the ring, a structure with two perpendicular symmetry planes for the dioxide derivatives is achieved. The higher symmetry can be related to the higher stability of the dioxides in comparison with the monoxides.

Aromaticity, and therefore cyclic conjugation, have a levelling effect on the differences in bond length between formal double and single bonds. Regarding the bond distances in Table 1, it can be seen that, in general, there is a good agreement between the calculated and the experimental distances. The minimal STO-3G* basis set seems to shorten the C—C double bonds that in a delocalized aromatic structure should be more alike [see thiophene (**1**) in Table 1]. However, the C—N double bond distances obtained using this basis set satisfactorily reproduce the aromaticity present in **2** and **3** according to their experimental bond distances.

In general, the C—S distances obtained are shorter than the experimental values when sulphur is divalent, but are larger than the experimental distances in the hypervalent S derivatives. This could be an effect of the quality of the basis set. A better agreement is observed between calculated and experimental N—S distances.

Occasionally, different types of bonds (C—C, C—N, etc.) can have the same length, and so another parameter, such as the bond order, is needed for a better evaluation of heteroaromaticity. An aromatic compound should exhibit a certain degree of uniformity in the bond orders of the ring. The following describes two different methods that we have used to calculate bond orders.

Calculations from bond order–bond length relationships

The inverse relationship between bond order and bond length has been extensively discussed and different equations have been developed.[12] Those of Paolini[12a] and Gordy[12b] were chosen for the present analysis. The calculated distances used for these analyses are those optimized by using the STO-3G* basis set.

Paolini's equation (1) describes a relationship between the bond order (ρ_P) and bond length (L_ρ), when compared with 'pure' single bonds (L_1):[12a]

$$L_\rho = L_1 - 0{\cdot}78(\rho_P^{0{\cdot}33} - 1). \qquad (1)$$

The single bond distances L_1 used here are those given by Paolini[12a] for the C—C (1·54 Å), C—N (1·47 Å) and C—S (1·81 Å) bonds. We also used the N—S (1·735 Å) bond found in Ref. 19. The bond orders, ρ_P, obtained are given in Table 2.

Gordy[12b] proposed a simple inverse square relationship between bond order (ρ_G) and bond length (L_ρ), given by the equation:

$$\rho_G = aL_\rho^2 - b \qquad (2)$$

where the constants a and b are characteristics of a given pair of atoms. The modified a and b parameters given by Paolini[12a] and those originally used by Gordy[12b] are almost linearly dependent [$y = 1{\cdot}061x - 0{\cdot}286$, correlation coefficient (r^2) = 0·986, standard error = 0·356]. By using a linear regression, we calculated a new set of modified a and b parameters with their corresponding 95% confidence errors

(Table 3). To obtain these parameters, we used the bond distances corresponding to the pure single bonds previously mentioned. The bond orders, ρ_G, obtained by using Gordy's equation with the new modified parameters are given in Table 2.

The results obtained from both equations are similar and, as expected, thiophene (**1**), isothiazole (**2**) and 1,2,5-thiadiazole (**3**) are described as aromatic structures. Note that both equations give very high bond orders (1·9) for the C_2—C_3 and C_4—C_5 bonds in thiophene and the C_4—C_5 bond in isothiazole. However, the values obtained for the other bonds in both rings are more consistent with aromaticity. For the monoxide (**4**, **5** and **6**) and dioxide (**7**, **8** and **9**) derivatives, double and single bond alternating rings resulted from the bond orders calculated with these equations.

Table 2. Bond orders obtained for all the compounds studied by using Paolini's (ρ_P) and Gordy's (ρ_G) equations[12]

Compound	Bond	ρ_P	ρ_G
1	C_2—$C_3 \equiv C_4$—C_5	1·94	1·88 ± 0·02
	C_3—C_4	1·46	1·44 ± 0·01
	S_1—$C_2 \equiv S_1$—C_5	1·53	1·54 ± 0·03
2	N_2—C_3	1·68	1·71 ± 0·02
	C_3—C_4	1·49	1·46 ± 0·01
	C_4—C_5	1·92	1·86 ± 0·02
	S_1—N_2	1·40	1·41 ± 0·02
	S_1—C_5	1·57	1·59 ± 0·03
3	N_2—$C_3 \equiv C_4$—N_5	1·67	1·70 ± 0·02
	C_3—C_4	1·48	1·45 ± 0·01
	S_1—$N_2 \equiv S_1$—N_5	1·44	1·45 ± 0·02
4	C_2—$C_3 \equiv C_4$—C_5	2·11	2·04 ± 0·02
	C_3—C_4	1·23	1·22 ± 0·01
	S_1—$C_2 \equiv S_1$—C_5	1·11	1·12 ± 0·01
5	N_2—C_3	1·87	1·90 ± 0·02
	C_3—C_4	1·22	1·20 ± 0·01
	C_4—C_5	2·13	2·06 ± 0·02
	S_1—N_2	0·99	0·99 ± 0·01
	S_1—C_5	1·09	1·10 ± 0·01
6	N_2—$C_3 \equiv C_4$—N_5	1·90	1·93 ± 0·02
	C_3—C_4	1·16	1·15 ± 0·01
	S_1—$N_2 \equiv S_1$—N_5	0·95	0·95 ± 0·01
7	C_2—$C_3 \equiv C_4$—C_5	2·16	2·09 ± 0·02
	C_3—C_4	1·15	1·15 ± 0·01
	S_1—$C_2 \equiv S_1$—C_5	1·01	1·01 ± 0·01
8	N_2—C_3	1·91	1·95 ± 0·02
	C_3—C_4	1·13	1·13 ± 0·01
	C_4—C_5	2·18	2·11 ± 0·02
	S_1—N_2	0·91	0·90 ± 0·01
	S_1—C_5	1·00	1·00 ± 0·01
9	N_2—$C_3 \equiv C_4$—N_5	1·94	1·97 ± 0·02
	C_3—C_4	1·09	1·08 ± 0·01
	S_1—$N_2 \equiv S_1$—N_5	0·87	0·86 ± 0·01

Table 3. Gordy's parameters a and b modified by linear regression, as explained in the text, and taking into account the error in a confidence interval of 95%

Bond	a	b
C—C	6·93 ± 0·13	1·92 ± 0·06
C—N	6·59 ± 0·19	2·05 ± 0·09
C—S	12·34 ± 0·76	2·76 ± 0·23
N—S	10·83 ± 0·52	2·61 ± 0·17

Bond orders from Mulliken population analysis

The bond orders were also computed from a Mulliken population analysis at the STO-3G*//STO-3G* and 6–31G*//STO-3G* levels of calculation. The bond orders for the rings were normalized by taking the averaged value obtained for the C—H bond for each compound as the 'pure' single bond (bond order = 1).

At the 6–31G*//STO-3G* level, the Mulliken population analysis underestimates the nature of S—C or S—N bonds. This estimation becomes even less accurate as the oxidation number of sulphur is increased. The results for C—C and C—N bonds reflect the conjugation for the S(II) compounds that are considered to be aromatic. A double–single alternating structure for the S(IV) and S(VI) derivatives is observed, which is in agreement with the results obtained with the equations used in the previous section.

At the STO-3G*//STO-3G* level the values obtained for C—C bonds in thiophene do not reflect the aromatic structure of this ring. For this reason, it is not worth comparing the results obtained for the other compounds.

In general, the results obtained from the Mulliken population analysis show that this method fails to provide good results regarding the bond order concept. This has been shown also by other workers.[28]

It must be noted that both methods depend strongly on the sort of calculation carried out. The former methods rely on the bond distances and the Mulliken population analysis on the electronic distribution obtained, and these properties in turn depend on the method and/or basis set used. Hence the results presented here have to be considered comparatively.

ELECTRONIC STRUCTURE AND PROPERTIES

The energies and atomic charges of the compounds studied at both the STO-3G*//STO-3G* and 6–31G*//STO-3G* levels of calculation are given in Table 4. In the S(II) structures, the introduction of one or two N atoms does not strongly affect the electronic distribution when compared with thiophene (see Table 4). Most of the charge density on **2** and **3** is located on the N atoms, and the S atom has a small net positive charge. In general, the C or S atoms adjacent to the N diminish their electron density. Thus, an

electron distribution similar to that of the aromatic compound **1** is observed in **2** and **3**.

However, the increment in the oxidation number of the sulphur atom causes considerable changes in the electronic structure and the uniformity in the charge distribution is lost. The introduction of one O atom double bonded to S leads to a sizable increment in the net positive charge of the S(IV) atom. The N atoms continue to bear most of the negative charge, their values being similar to those obtained for the S(II) derivatives. The introduction of a second double-bonded O atom increases the positive charge on the S atom, but not as dramatically as with the first one. Moreover, this second O atom does not affect the charge on the N atoms.

A similar insight is provided by an analysis of the dipole moments (see Table 5). The monoaza derivatives (**2, 5** and **8**) present large y-components of the dipole moment (μ_y) owing to the change in the symmetry caused by the introduction of an N atom. In the case of the monoxide structures, a z-component μ_z appears owing to the non-planarity of the ring. For the sake of simplicity, a single dipole moment component for all the compounds will be analysed. Since thiophene, the aromatic reference compound, has a dipole moment with only an x-component, μ_x will be the component

Table 4. Energies and atomic charges for all the compounds studied obtained at STO-3G*//STO-3G* and 6–31G*//STO-3G* levels of calculation (X = N or C)

Level	Compound	E (hartree)	S_1	X_2	C_3	C_4	X_5	O_a	O_b
STO-3G*//STO-3G*	**1**	−545·139645	15·868	6·107	6·082	6·082	6·107	—	—
	2	−560·905346	15·789	7·265	5·974	6·097	6·094	—	—
	3	−576·671374	15·704	7·244	5·989	5·989	7·244	—	—
	4	−618·930390	15·708	6·091	6·058	6·058	6·091	8·307	—
	5	−634·700465	15·644	7·241	5·942	6·072	6·081	8·285	—
	6	−650·471307	15·578	7·224	5·955	5·955	7·224	8·261	—
	7	−692·771643	15·616	6·070	6·048	6·048	6·070	8·254	8·254
	8	−708·543755	15·572	7·214	5·929	6·062	6·056	8·233	8·233
	9	−724·314689	15·526	7·193	5·942	5·942	7·193	8·211	8·211
6—31G*//STO-3G*	**1**	−551·288924	15·696	6·414	6·177	6·177	6·414	—	—
	2	−567·278570	15·525	6·570	5·968	6·225	6·399	—	—
	3	−583·267524	15·363	7·539	6·015	6·015	7·539	—	—
	4	−626·059383	14·984	6·473	6·144	6·144	6·473	8·740	—
	5	−642·056503	14·878	6·584	5·931	6·181	6·460	8·710	—
	6	−658·052294	14·787	6·559	5·961	5·961	6·559	8·676	—
	7	−700·898236	14·460	6·486	6·137	6·137	6·486	8·658	8·658
	8	−716·897380	14·391	6·574	5·926	6·171	6·464	8·634	8·634
	9	−732·891129	14·335	6·542	5·950	6·542	5·950	8·608	8·608

Table 5. Dipole moments (in debye) with their x, y and z component values for all the compounds studied by a 6–31G*//STO-3G* calculation

Compound	Dipole moment	X-component	Y-component	Z-component
1	0·781	0·781	0·000	0·000
Exp. **1**[a]	0·55	—	—	—
2	2·903	1·426	2·528	0·000
Exp. **2**[a]	2·4 ± 0·2	—	—	—
3	2·006	2·006	0·000	0·000
Exp. 3[a]	1·58 ± 0·2	—	—	—
4	5·009	4·815	0·000	1·380
5	6·065	5·369	2·520	1·268
6	5·968	5·858	0·000	1·142
7	5·790	5·790	0·000	0·000
8	6·898	6·390	2·597	0·000
9	6·926	6·926	0·000	0·000

[a] Experimental dipole moments for compounds **1**[20c], **2**[19] and **3**.[19]

considered for comparison. The schematic representation of μ_x, μ_y and μ_z for the nine compounds is shown in Figure 3.

On passing from S(II) to S(IV) compounds, a very large increment in μ_x is observed. Taking into account the charge distribution, this increment could reflect a separation of charges. Such a situation, as in an ylide, occurs because the X—C—C—X (X = C or N) moiety has an averaged negative charge, whereas the S atom presents a net positive charge. The electronic delocalization in the S(II) aromatic derivatives would be responsible for their small μ_x value. Considering that the electrons taken from the S atom by the oxygen were those involved in the π delocalization (e.g. in

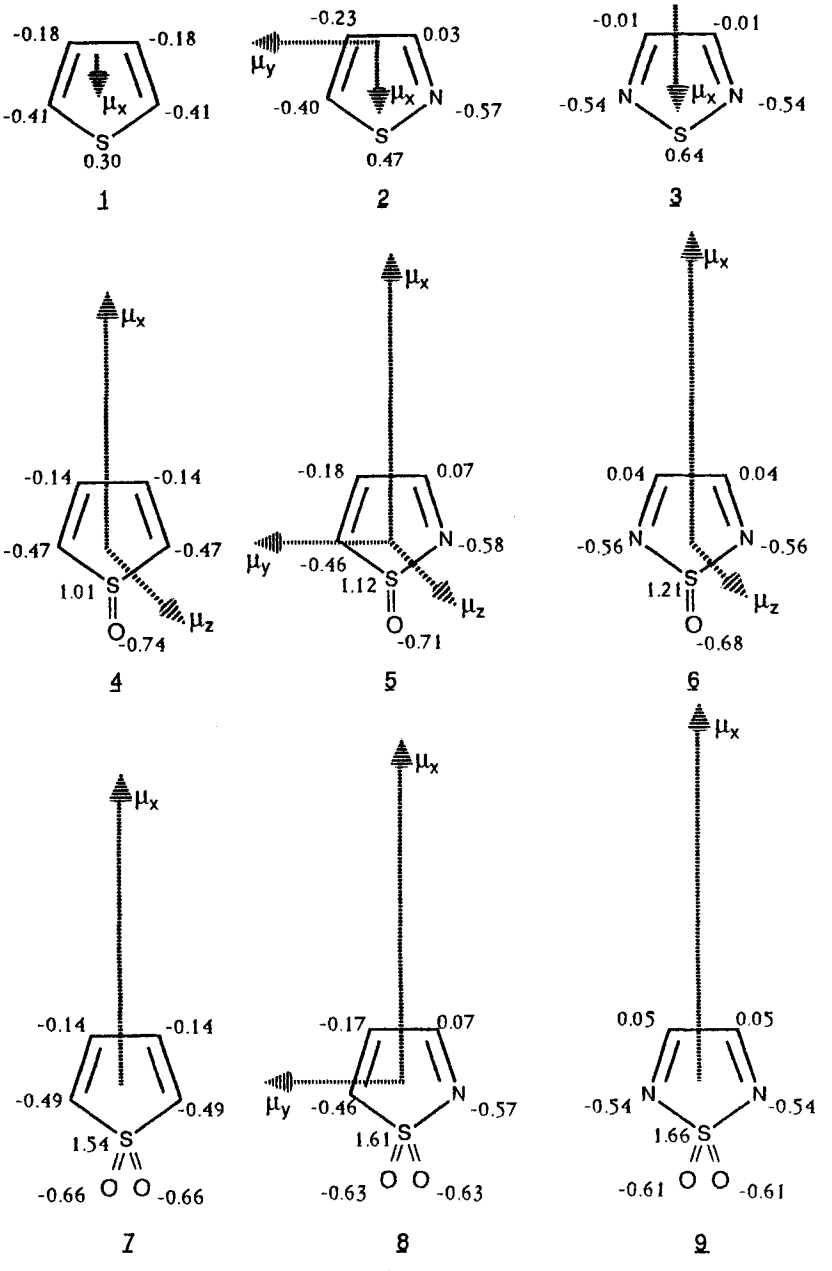

Figure 3

thiophene), one could associate the increment in μ_x to aromaticity. Nevertheless, it could be interpreted that this increment in μ_x for the oxides is due to the electronegativity of the O atom, but this change is not so important after introducing a second O atom.

The introduction of this second O atom increases μ_x uniformly for the three dioxides ($\Delta = 1{\cdot}0$). This increment is smaller than those obtained for the monoxides. Hence the proposed ylide structure would be present also in the S(VI) derivatives, and the large change in μ_x on passing from the S(II) to S(IV) and S(VI) derivatives would be due to the loss of aromaticity.

PARTICIPATION OF THE d-ORBITALS OF SULPHUR IN SULPHUR BONDS

In order to increase the resonance stabilization of thiophene, Pauling[27c] proposed that the d-orbitals on sulphur could be hybridized into the aromatic sextet. In our case, an inspection of the MOs of thiophene (**1**) indicates that d-orbital participation is not significant in the ground state. Moreover, an analysis of the three π-type occupied MOs reveals that the S(II) atom contributes only p_z-orbitals to the π system. This same situation is observed for the other S(II) derivatives, **2** and **3**.

In the case of the derivatives with hypervalent S atoms, there are a number of hybrid orbital combinations that can account for the S contribution to a π system. The empty d-orbitals of S(IV) and S(VI) have always been considered to be involved in the conjugation since they can be filled by delocalized electrons from the π system.

The MOs of the monoxides (**4**, **5** and **6**) present a high mixing of orbitals. However, whereas pure π-type occupied MOs could not be found, the p_z-orbital participation seems to be the most important in the X—C—C—X (X = C or N) moiety, indicating a certain π-conjugation in this part of the molecules. Nevertheless, the participation of sulphur d-orbitals is not significant in the bonding with this moiety. In fact, this moiety seems not to be π conjugated with the S(IV) atom, in contrast to thiophene.

The analysis of the MOs of the dioxides **7**, **8** and **9** shows that there are three π-type occupied MOs as in the S(II) derivatives. As in these aromatic compounds, the d-orbital participation in the S(VI) derivatives is not significant for any atom in the ring (d-orbital coefficients $<0{\cdot}019$ in the HOMO and $<0{\cdot}12$ in the other two π-type MOs). There is some d-orbital participation of sulphur when bonding C and N, but even in the case of S—N (the largest one with a coefficient of $0{\cdot}1252$) this contribution is not very important. However, for the dioxides there is only p_z-orbital participation for the C and the N atoms (coefficients $\approx 0{\cdot}255$) and the S(VI) atom does not contribute to the π system with any p_z-orbital. Accordingly, it is not possible to speak of total π delocalization in any of the three rings. A better description for these S(VI) derivatives would be as ylides where a X—C—C—X (X = C or N) moiety is π-conjugated and σ-bonded to an SO_2 group that is not involved in the delocalization.

CONCLUSIONS

Regarding the geometrical criteria, only compounds **1**, **2** and **3** can be considered to be aromatic since they are planar and present a certain uniformity in the bond orders of the ring. The monoxides are non-planar and, like the planar dioxides, exhibit alternating double bond structures.

The introduction of one or two N atoms adjacent to an S(II) atom does not strongly affect the charge distribution in these five-membered rings. Thus, by comparison with the electron structure of thiophene, compounds **2** and **3** may also be considered to be aromatic. However, the increment in the oxidation number of the S atom ($S \rightarrow SO \rightarrow SO_2$) strongly changes the charge distribution in the ring, leading to a break in the uniformity of the distribution characteristic of the S(II)-containing compounds.

The S(II) derivatives **1**, **2** and **3** present a small μ_x component that indicates electron delocalization in the rings. In contrast, the very large μ_x value obtained for the remaining compounds suggests ylide structures produced as a consequence of the increment in the oxidation number of the S atom.

The analysis of the MOs of sulphur confirms that only thiophene (**1**), isothiazole (**2**) and 1,2,5-thiadiazole (**3**) can be considered to be aromatic since only they show p_z-orbital participation in the π system. No d-orbital participation in the delocalized system is observed in any of the compounds studied. The introduction of S atoms with higher oxidation state [S(IV) and S(VI) derivatives] causes the breaking of the delocalized π system. According to the inspection of the MOs, these compounds might be better described as ylide structures, where the X—C—C—X (X = C or N) moiety is conjugated and σ-bonded to the SO or SO_2 groups.

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