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Molecular Orbital Study of Some Heterocycles Containing Nitrogen and Sulphur

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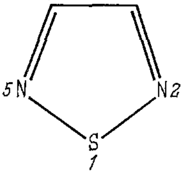
A systematic study of 1, 2, 5-Thiadiazole (I), 2, 1, 3-Benzothiadiazole (II) and the recently synthesised Naphtho[2, 3-*c*]-1, 2, 5 thiadiazole (III) has been made using the Hückel molecular orbital theory (HMO). Stability and reactivity of these molecules as predicted by HMO calculations are in agreement with experimental observations. For (I) and (II) bond lengths are known and excellent agreement with theory has been shown. Spin densities calculated for the radical anion of (II) are in good agreement with experimental data. Bond lengths in (III) and its reactivity as well as the spin densities for its radical anion are predicted.

Es wurde eine systematische HMO-Studie von 1, 2, 5-Thiadiazol (I), 2, 1, 3-Benzothiadiazol (II) und dem kürzlich synthetisierten Naphto-[2, 3-*c*]-1, 2, 5-thiadiazol (III) durchgeführt. Die HMO-Berechnung der Stabilität und Reaktivität ist in Übereinstimmung mit den experimentellen Ergebnissen. Theoretische Bindungslängen für (I) und (II) und Spindichten für (II) sind ebenfalls in Übereinstimmung mit den Experimenten, Bindungslängen und Spindichten für (III) werden vorausgesagt.

Utilisant la méthode des orbitales moléculaires de Hückel (HMO) nous avons étudié systématiquement les 1, 2, 5-thiadiazole (I), 2, 1, 3-benzothiadiazole (II) et le naphto [2, 3-*c*]-1, 2, 5 thiadiazole (III) récemment synthétisé. La stabilité et la réactivité de ces molécules, telles que la théorie les prédit, sont en bon accord avec les données expérimentales. Les longueurs des liaisons de (I) et (II) sont connues et sont en bon accord avec la théorie. Les densités de spin calculées pour l'anion radicalaire de (II) sont en bon accord avec l'expérience. On prédit les longueurs de liaison et la réactivité de (III) ainsi que les densités de spin de son anion radicalaire.

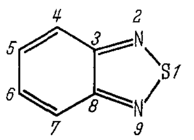
Introduction

Although (I) and (II) are known to be stable it is only recently that Cava and Schlessinger [2] reported the synthesis of (III). Various properties of (I), (II) and (III) have been examined by employing the *p*-orbital [6] model for sulphur in the simple HMO method [11].



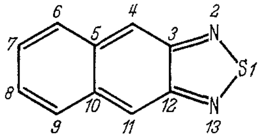
I

Fig. 1



II

Fig. 2



III

Fig. 3

Fig. 1. 1, 2, 5-Thiadiazole
Fig. 2. 2, 1, 3-Benzothiadiazole
Fig. 3. Naphtho [2, 3-*c*] —1, 2, 5-thiadiazole

Parameters for MO Calculations

The following Hückel parameters are required in the MO calculations: $h_{\dot{\mathrm{N}}}$, $h_{\ddot{\mathrm{S}}}$, $k_{\mathrm{C-N}}$ and $k_{\mathrm{N-S}}$. In the MO calculations reported here values of $h_{\dot{\mathrm{N}}} = 0.5$ and

Table 1. *Electron Densities, Frontier Electron Densities and Cation Localization Energies in* (I), (II) *and* (III)

Compound	Position r	π-Electron density	Frontier electron density[a]	Cation localization energy in β
(I)	1	1.5181		
	2	1.2447		
	3	0.9961		
(II)	1	1.4371		
	2	1.2725		
	3	0.9937		
	4	1.0102	0.1442	2.2918
	5	1.0049	0.0419	2.3956
(III)	1	1.4160		
	2	1.2788		
	3	0.9915		
	4	1.0147	0.1807	2.0046
	5	1.0025		
	6	1.0020	0.0832	2.2220
	7	1.0021	0.0436	2.4108

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[a] Frontier electron density $= C^2_{m,r}$ where $C_{m,r}$ is the co-efficient of the rth atomic orbital in highest occupied MO. Since electrophilic reactions have been considered the frontier orbital is the highest occupied MO.

Table 2. *Bond-Orders and Bond Lengths in* (I), (II) *and* (III)

Compound	Bond	Calculated mobile bond order	Calculated bond length in Å	Observed bond length in Å
(I)	1 – 2	0.536	1.622	1.631
	2 – 3	0.676	1.320	1.328
	3 – 4	0.680	1.395	1.42
(II)	1 – 2	0.579	1.615	1.60
	2 – 3	0.548	1.345	1.34
	3 – 4	0.566	1.415	1.46
	4 – 5	0.723	1.387	1.29[a]
	5 – 6	0.603	1.409	1.46
	3 – 8	0.528	1.422	1.41
(III)	1 – 2	0.588	1.612	
	2 – 3	0.524	1.350	
	3 – 4	0.617	1.406	
	4 – 5	0.605	1.408	
	5 – 6	0.535	1.421	
	6 – 7	0.738	1.384	
	7 – 8	0.585	1.412	
	3 – 12	0.495	1.428	
	5 – 10	0.485	1.430	

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[a] This experimental value appears to be rather anomalous.

$k_{\mathrm{C-N}} = 0.8$ were used [*12*]. The value of $h_{\ddot{\mathrm{S}}} = 1.0$ suggested by Gerdil and Lucken [*6*] was adopted. This value of $h_{\ddot{\mathrm{S}}}$ can be justified on the ground that the difference $h_{\ddot{\mathrm{X}}} - h_{\dot{\mathrm{X}}}$ is expected [*15*] to be of the same order as ω, the parameter used in the Wheland-Mann procedure. Since we have $h_{\dot{\mathrm{S}}} = \chi_{\mathrm{S}} - \chi_{\mathrm{C}} = 2.5 - 2.5 = 0$, where χ_{S} and χ_{C} are electronegativities of sulphur and carbon respectively, and ω is of the order of $1 - 1.5$, we get $h_{\ddot{\mathrm{S}}} = 1.0$. In order to arrive at a suitable value for $k_{\mathrm{N-S}}$ we made use of the overlap integrals [*8*] for N–S($2p\pi - 3p\pi$) and C–C ($2p\pi - 2p\pi$) bonds at appropriate bond distances. Thus [*9*]

$$k_{\mathrm{N-S}} = \beta_{\mathrm{N-S}}/\beta_{\mathrm{C-C}} = [S_{\mathrm{X}}/(1 + S_{\mathrm{X}})]/[S_0/(1 + S_0)]$$

where S_{X} is the overlap integral for the N–S bond in 1, 2, 5-Thiadiazole while S_0 is the overlap integral for C–C bond in benzene and $\beta's$ refer to resonance integrals. The calculated value of S_{X} and S_0 being 0.157 and 0.245 respectively we get a value of $k_{\mathrm{N-S}} = 0.69$.

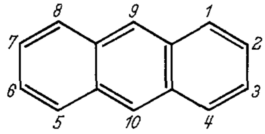
Using the values of $h_{\dot{\mathrm{N}}} = 0.5$, $h_{\ddot{\mathrm{S}}} = 1.0$, $k_{\mathrm{C-N}} = 0.8$ and $k_{\mathrm{N-S}} = 0.69$ MO calculations were carried out for (I), (II) and (III). Tab. 1 summarizes our results for electron densities, frontier electron densities and cation localization energies in (I), (II) and (III). Calculated bond-orders and bond lengths in (I), (II) and (III) are given in Tab. 2 along with available experimental data [*3*, *7*].

Reactivity of (I), (II) and (III) in Electrophilic Reactions

In (II) it can be seen that π-electron density value for positions 4 and 7 is significantly greater than that for positions 5 and 6 and this result is in good agreement with experimental studies on electrophilic substitution [*4*]. The same conclusion can also be reached from a comparison of frontier electron densities of various positions of (II). According to the frontier electron theory [*5*] electrophilic substitutions occur at the position with highest $C^2_{m,r}$ value, where $C_{m,r}$ is the coefficient of the rth atomic orbital in the highest occupied molecular orbital. It can be seen that out of 4, 5, 6 and 7 positions (all carbon positions), $C^2_{m,r}$ is maximum for 4 and 7 positions. A comparison of cation localization energy also leads to the same conclusion. It has been postulated [*17*] that electrophilic substitution will occur at the position for which cation localization energy is minimum. In the molecule (II) the cation localization energy, infact, is minimum for 4 and 7 positions. Out of all the carbon positions in (III) the electron density value is highest for 4 and 11 positions. Consequently electrophilic reactions are predicted to occur at 4 and 11 positions. A consideration of frontier electron density values and cation localization energies for various positions in (III) also leads to the same conclusion. Out of all carbon positions in (III) frontier electron density value is maximum and cation localization energy is minimum for positions 4 and 11. A consideration of frontier electron densities and cation localization energies for 6 and 7 positions in (III) suggests 6 position to be more reactive than 7 in electrophilic reactions, but a consideration of electron density values suggests 6 and 7 positions to be of comparable reactivity. Which conclusion is correct can only be seen when experimental results will be available for (III).

Delocalization Energies and Stability

It has been pointed out by Cava and Schlessinger [*2*] that (III) is a highly stabilized system like anthracene (IV). This fact can also be seen from MO point of view by comparing our π-delocalization energy for (III) (4.753 β) with that of anthracene (5.314 β) [13]. The calculated π-delocalization energies of (I) and (II) are 1.414 β and 3.122 β respectively where β is the resonance integral for adjacent carbon atoms in benzene. The delocalization energies [13] of benzene and naphthalene being 2.000 β and 3.683 β respectively it is clear that the stabilities of (I) and (II) are comparable with those of benzene and naphthalene respectively.



IV

Fig. 4. Anthracene

Reactivity in Diels-Alder Reaction

BROWN [1] has suggested a reactivity index for explaining the reactivity of dienes in Diels-Alder reactions. He has pointed out that if $L_{p_{r,s}}$ is greater than 3.6 for positions r and s no adduct will be formed. Our calculations yield the following $L_{p_{r,s}}$ values for (III).

$$L_{p_{6,9}} = 3.631\,\beta$$
$$L_{p_{4,11}} = 3.339\,\beta\,.$$

Thus in (III) our $L_{p_{r,s}}$ values predict that Diels-Alder reaction will occur at positions 4 and 11 and has infact been observed experimentally by CAVA and SCHLESSINGER [2]. $L_{p_{9,10}}$ in (IV) is 3.314β [14] while for the corresponding positions in (III) $L_{p_{4,11}}$ is 3.339 β. Hence we may conclude that (III) is a less reactive diene compared to (IV) in Diels-Alder reaction. This also is in agreement with experimental results of CAVA [2]. For (II) $L_{p_{4,7}} = 3.708\,\beta$. So it is not expected to form an adduct with maleic anhydride in Diels-Alder reaction.

Spin Densities

Recently e.s.r. spectrum of the radical anion of (II) has been recorded by STROM and RUSSELL [16]. The ratio of spin densities $\varrho_{C-4}/\varrho_{C-5}$ in the radical anion of (II) reported by STROM and RUSSELL is 1.7 and that is in good agreement with the value 1.8 obtained from our calculations. Using the simple odd electron density relation $\varrho_r = C^2_{m+1,r}$ where ϱ_r is the spin density on atom r and $C_{m+1,r}$ is the coefficient of the rth atomic orbital in the MO occupied by the odd electron, we have calculated the spin density values for the radical anion of (III). The ϱ_r values are 0.1130, 0.0413 and 0.0253 for positions 4, 6 and 7 respectively. Since no experimental e.s.r. spectrum of the radical anion of (III) has so far been obtained a comparison can not be made for the present. Efforts in this direction would be worth while.

Bond-Orders and Tetracovalent Character of Sulphur

Good agreement between experimental bond lengths and calculated bond lengths can be seen from Tab. 2. N–S and C–N bond lengths were obtained from calculated bond orders by using appropriate bond order-bond distance curves.

C–C bond lengths were obtained by employing the relation [*10*] $R(p) = 1.517 - 0.18p$ where $R(p)$ is the length of the bond in Å and p is the mobile bond order. It can be seen that the mobile bond order for the N–S bond increases as one goes from (I) to (III). Infact CAVA and SCHLESSINGER [*2*] have commented about the significant degree of tetracovalent character of sulphur in (III). From the available experimental data it can be seen that the C–N bond distance increases as one goes from (I) to (II) and this conclusion is also reached from our calculations. Since experimental data are not available for bond lengths in (III) no comparison can be made at present.

Conclusion

It is seen that simple HMO method with a well chosen set of parameters can explain to a great extent the different chemical and physical properties of (I), (II) and (III). Advanced MO calculations for these molecules are in progress and these may throw some light on the spectral behaviour of these compounds.

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