

singlets (Fig. 1). In cases where this signal could not be resolved at 60 Mc/s (hemiacetals of less sterically hindered alcohols such as 2-butanol) it was possible to resolve this signal into two components by use of 100 Mc/s spectra. The occurrence of epimerization was demonstrated by recording the NMR-spectrum of the previously mentioned hemiacetal of 3,3-dimethyl-2-butanol as a function of time (Fig. 2). As shown in the figure, the mole fraction  $X_A$  of the most shielded  $H_x$ -proton changed from 0.72 to 0.50 in 1440 min. No further change in the mole fraction was observed after 1440 min, in contrast to the reaction followed by UV which was complete after 10 min. The mole fraction of the two diastereomers was determined by measuring (by use of a planimeter) the areas of the two signals. To make this measurement possible the signals were separated from each other by drawing a vertical line from the crossing point between the two signals to the base line. It is interesting to observe (Fig. 1) that the mole fraction at equilibrium for three different hemiacetals is approximately 0.5. This means that the free energy difference between the two

diastereomeric hemiacetals is approximately zero, contrary to the energy difference between their corresponding transition states. In order to obtain a better understanding of the epimerization process, a study of the half lives of various hemiacetals as a function of the steric bulk of the groups surrounding the asymmetric centre is planned.

*Experimental.* NMR Spectra were recorded on a Varian A-60 A spectrophotometer in  $CCl_4$  solution with TMS as internal standard at 25°. The concentration of chloral and the alcohols were both  $5 \times 10^{-1}$  M and the concentration of acetic acid was  $10^{-2}$  M in the experiments shown in Fig. 1. For the experiments shown in Fig. 2, no acetic acid was added and the concentrations of chloral and 3,3-dimethyl-2-butanol were both  $5 \times 10^{-1}$  M.

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## An SCF MO Study of Two Isomeric Thiadiazoles

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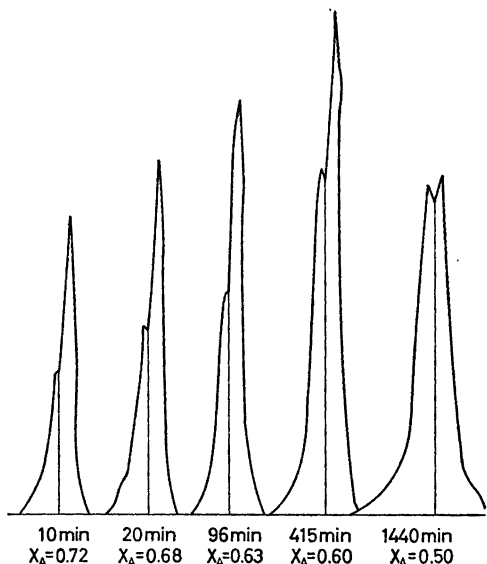


Fig. 2. Time dependence of the NMR-signal at 4.0  $\tau$  of the chloral hemiacetal of 3,3-dimethyl-2-butanol. These spectra were recorded with a sweep-width of 50 cps. 1 mm =  $8.35 \times 10^{-3}$   $\tau$ .  $X_A$  is the mole fraction of the most shielded diastereomer.

From a theoretical point a view the electronic structure of the monocyclic thiadiazoles is of considerable interest.<sup>1-3</sup> Previous calculations, performed within the Hückel-approximation, have made possible a discussion of some of the molec-

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ular properties related to the  $\pi$ -electron distributions.<sup>2,3</sup>

The purpose of the present note is to present a comparative study of the  $\pi$ -electron structures of the ground states of the symmetrical isomers 1,3,4- and 1,2,5-thiadiazole, called (I) and (II), respectively, by using the well-known Pariser-Parr-Pople approximation<sup>4-6</sup> in the SCF theory.

Our calculations are based on the assumption that the sulphur atom contributes a  $3p\pi$ -orbital to the conjugate system.

The semi-empirical parameters have been evaluated in the following way:

The core resonance integrals,  $\beta_{\mu\nu}$ , were determined by use of the simple relation

$$\beta_{\mu\nu} = \beta_0 S_{\mu\nu} / S \quad (1)$$

where  $S_0$  and  $\beta_0$  are the overlap and resonance integrals for benzene. The latter was assumed to be  $-2.39$  eV.<sup>5,7</sup> The evaluation of overlap integrals was based on Slater type orbitals, and experimental bond distances.<sup>14,15</sup>

The diagonal elements of the core operator were decomposed according to the method of Goepfert-Mayer and Sklar:<sup>8</sup>

$$\alpha_\mu = W_\mu - \sum_{\nu \neq \mu} \gamma_{\mu\nu} \quad (2)$$

In (2)  $n_\nu$  is the number of  $\pi$ -electrons contributed to the system by atom  $\nu$ .  $\gamma_{\mu\nu}$  is the Coulomb repulsion integral between electrons centered at atoms  $\mu$  and  $\nu$ , and  $W_\mu$  may be interpreted as an approximation to the valence state ionization potential for atom  $\mu$ . In our calculations we have used the values  $W_C = -11.54$  eV,  $W_N = -14.32$  eV, and  $W_S = -12.50$  eV.

These values are not quite appropriate for the valence states considered relevant here, but we found it to be an advantage to have  $W$ -values referring to corresponding states for all the atoms. Furthermore, the changes in the values due to rearrangements of the underlying  $\sigma$ -system are very small.<sup>10</sup>

The one-center two-electron integrals were evaluated by use of the relation<sup>5</sup>

$$\gamma_{X^0} = (IP)_X - (EA)_X \quad (3)$$

where the atomic IP-values are those referred to above, and EA represents the electron affinity for the corresponding states. The values obtained are  $\gamma_S^0 = 9.80$  eV,  $\gamma_C^0 = 10.53$  eV, and  $\gamma_N^0 = 12.73$  eV. The two-center two-electron integrals were estimated by means of the uniformly charged sphere approximation,<sup>5</sup> with orbital exponents based on Slater's rules.

The bond orders and  $\pi$ -electron charges obtained by the calculations, which were performed on a UNIVAC 3300 computer, are collected in Table 1 and Table 2, respectively. For numbering of atoms see Fig. 1.

The calculated bond orders were in the usual way employed for a prediction of bond distances. For the C—C bond in (II) we used the empirical linear relation

$$R_{CC} = 1.517 - 0.18p_{CC} \quad (4)$$

discussed previously by one of us.<sup>11</sup> A similar relation for C—N bonds has recently been suggested<sup>12</sup>

$$R_{CN} = 1.458 - 0.18p_{CN} \quad (5)$$

Table 1. Calculated bond orders for 1,3,4-thiadiazole (I) and 1,2,5-thiadiazole (II). Values obtained by Hückel calculations (HMO) are included for comparison.

Bond	Molecule I		Molecule II	
	SCF	HMO <sup>a</sup>	SCF	HMO
1-2	0.3392	0.464	0.3109	0.468 <sup>a</sup> 0.536 <sup>b</sup>
2-3	0.8902	0.787	0.7452	0.780 0.676
3-4	0.3099	0.526	0.3830	0.541 0.680

<sup>a</sup> Ref. 2; <sup>b</sup> Ref. 3.

Table 2. Calculated  $\pi$ -electron charges on the different atoms. In electron units.

Atom	Molecule I	Molecule II
	1	+0.1647 (S)
2	+0.1702 (C)	-0.5227 (N)
3	-0.2525 (N)	+0.3899 (C)



Fig. 1. Numbering of atoms in 1,3,4-thiadiazole (I) and 1,2,5-thiadiazole (II).

By using the calculated bond order and the measured N—N distance in pyridazine, we obtain the following relation<sup>13</sup>

$$R_{\text{NN}} = 1.424 - 0.18p_{\text{NN}} \quad (6)$$

Application of these formulae gives the bond distances presented in Table 3, where also experimental values obtained by microwave spectroscopy<sup>14,15</sup> are included for comparison.

Table 3. Calculated and observed bond distances. In Å units.

Bond	Molecule I		Molecule II	
	$R_{\text{calc.}}$	$R_{\text{obs.}}^a$	$R_{\text{calc.}}$	$R_{\text{obs.}}^a$
1—2	—	1.7205	—	1.631
2—3	1.298	1.3024	1.324	1.328
3—4	1.368	1.3710	1.448	1.420

Observed  $R$ -values: <sup>a</sup> Ref. 14; <sup>b</sup> Ref. 15.

The values in Table 1 clearly show that the low bond orders obtained by the Hückel approximation are decreased by the SCF calculation, and the high bond orders are correspondingly increased. This accentuation of alternating high and low  $\pi$ -electron densities is rather satisfactory due to the presence of hetero-atoms with different electronegativities. The agreement between calculated and observed distances shown in Table 3 is very satisfactory for all the bonds considered except for the C—C bond in (II). Also here the agreement has to be considered as acceptable. Particularly the observed difference between the N—C bond distances in the two isomers is exactly reproduced by our calculations.

The predicted vertical ionization potentials are 12.26 eV and 10.00 eV for (I) and (II), respectively. These values are most certainly too high, due to the fact that the applied  $W_{\mu}$  values are based on atomic valence state energies. However, the calculated difference should be rather realistic. To the authors' knowledge no experimental values are available.

The calculated atomic charges presented in Table 2 indicate a high degree of polarity in both isomers. The predicted  $\pi$ -electron dipole moments are 3.86  $D$  and 2.92  $D$  for (I) and (II), respectively. The only observed value,<sup>16</sup> 3.28  $D$  for (I), is qualitatively in agreement with the calculated value. The values obtained for the  $\pi$ -electron charge distributions permit us to conclude that (II) should be more sensitive to both nucleophilic and electrophilic attacks than (I). This conclusion is in accordance with available experimental information.<sup>1,2</sup>

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