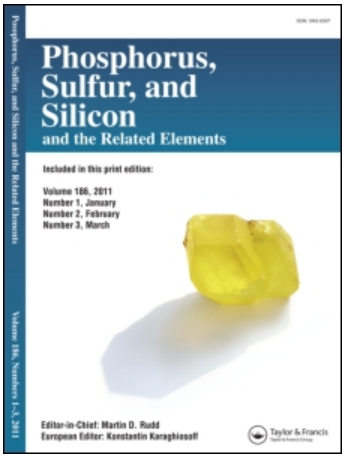

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ELECTRONIC STRUCTURE OF SOME SUBSTITUTED AZOLIDINES. CNDO/2, NMR AND VIBRATIONAL SPECTROSCOPIC STUDIES.

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The ^{1}H and ^{13}C chemical shifts, characteristic vibrational frequencies and force constants for some substituted azolidines are correlated with the results of the CNDO/2 calculations. The influence of the exo and endo heteroatoms on the electronic structure of the heterocyclic ring are discussed.

INTRODUCTION

The special attention given in recent years to the spectroscopic and structural studies of heterocyclic molecules of the type, Z—CH_2CH_2—Y—C=X, where Z,Y may be O, S, Se, NH or CH_2 and X = O, S, Se seems to stem from their property to exhibit pseudo rotation[1,2] and their ability to provide potential binding sites for metal ions in physiological systems[3] as well as for their good coordinating properties.[4-6] The compounds presently considered are oxazolidine-2-one (Oxo; X=Z=O, Y=NH), oxazolidine-2-thione (Oxt; X=S, Y=NH, Z=O), thiazolidine-2-thione (Tzdt; X=S, Y=NH, Z=S), thiazolidine-2-selone (Tzse; X=Se, Y=NH, Z=S) and imidazolidine-2-thione, commonly referred to as ethylenethiourea (Etu; X=S, Y=Z=NH). We recently investigated[7-11] from vibrational spectroscopic technique, the influence of exo and endo heteroatoms on the ring properties of these heterocyclic molecules. We report here the proton and carbon-13 magnetic resonance spectra and the results of the semiempirical CNDO/2 calculations. The aim of the present work is to discuss the vibrational and ^{1}H and ^{13}C NMR spectroscopic data in terms of the computed bond orders and charge densities. The CNDO/2 type of quantum mechanical method was employed since a striking similarity in the pi charge values are reported with CNDO/2 and ab initio methods.[12,13] The previous pertinent works are the CNDO/S calculations by Guimon *et al.*[14,15] and Arbelot *et al.*,[16] who focused their attention on the electronic and photoelectron spectra of some thiocarbonyl based substituted azolidines.

RESULTS AND DISCUSSION

The computed pi bond orders and the relevant atomic charges for the azolidines considered are compiled in Table I. It was observed that the stabilization in terms of the total molecular energy produced by O, NH and S in the position α to the thiocarbonyl group increased in the order NH>O>S, which is in the increasing order of mesomeric electron releasing tendencies.

TABLE I

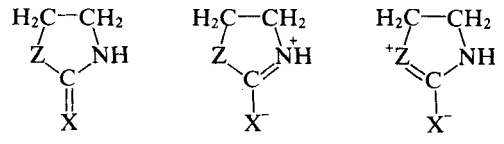
CNDO/2 results for some substituted azolidines.

Compound	Bond order C=X	Bond order C—N(Y)	Bond order C—Z	Charge density X	Charge density N(Y)	Charge density C	Charge density Z	ν(NH) (cm^{-1})	K(NH) (mN/m)
Oxo (X=O, Z=O)	0.758	0.520	0.315	−0.419	−0.200	0.517	−0.254	3260	5.40
Etu (X=S, Z=NH)	0.547	0.536	0.536	−0.462	−0.151	0.287	−0.151	3250, 3275	5.30
Oxt (X=S, Z=O)	0.603	0.595	0.392	−0.402	−0.135	0.324	−0.182	3205	5.15
Tzdt (X=S, Z=S)	0.612	0.645	0.248	−0.365	−0.044	0.171	−0.047	3130	4.95
Tzse (X=Se, Z=S)	—	—	—	—	—	—	—	3100	4.85

ν—stretching; K—stretching force constant

Bond order: The following three canonical forms may be said to contribute predominantly to the bonding of azolidines. For these systems, a direct correlation between C=S and C—N bond orders as in simple acyclic thionamides, S=C(—)—N<, is difficult. In amides, the C—N pi bond order increases with decreasing C=X double bond order in the sequence X = O<S. From Table I, it is however observed that both C=S and C—N bond orders (excepting Oxo) show variation in the same direction. This difference could be attributed to the effect of different endo heteroatoms at the α-position in these molecules. The C—N(Y) and C—Z bond orders (excepting Oxo) register opposite trends; the C—N bond order increases as the endo heteroatom varies in the order N, O and S, while the corresponding C—Z bond order gradually decreases. The C—Z bond which is usually written as a single bond has some partial double bond character varying in the sequence, Etu>Oxt>Tzdt, which also parallels the mesomeric electron releasing ability of the atom at the α-position.

The bond order of the C=S grouping increases in the sequence Etu<Oxt<Tzdt in the decreasing mesomeric electron releasing tendency of the atom at α-position. A similar trend has been noted[21] for dithiocarbamates, xanthates and trithiocarbonates ($X—CS_2^-$, $X=NR_2$, —OR and —SR, respectively). The C=S bond order of Etu is the lowest (0.547); this could be attributed to the two mesomeric nitrogens at the α-positions of Etu, thus enhancing the contribution of the charge-separated structures (b) and (c). From C=S and C—N bond length values, it is estimated that in Etu structures (b) and (c) contribute **Ca.** 40% each to the bonding.[20]



(a) (b) (c)

FIGURE 1 Canonical forms.

Charge density: The calculated charge densities reveal that the charge on the exocyclic thiocarbonyl sulfur decreases along Etu, Oxt and Tzdt; the charge on nitrogen also decreasing in the same order. That is, an increasing positive charge on the nitrogen atom is indicated along the series. The large decrease in the N—H stretching frequency from Oxt to Tzdt and Tzse can be ascribed to the increasing positive charge on nitrogen with decreasing tendency of the exocyclic heteroatom to form double bond with carbon.[22,23] Further, the N—H stretching force constants also show a gradual decrease from Oxo to Tzse (5.40 to 4.85 mN/m), as is to be expected. It is to be noted that the extent of decrease in the N-H frequency on replacement of an exo heteroatom is smaller while a similar substitution in the ring produces a relatively larger shift (Table I) concordant with the calculated negative charge on nitrogen. Thus the variation in the N—H stretching frequency is easily explained by variation in the electronic structure of the bond.

In Table II, ^{1}H and ^{13}C chemical shift values are listed. Downfield shift in the N—H proton resonance in the increasing order of positive charge on nitrogen is observed (excepting for Oxo). The NH proton resonance of Etu appears at relatively upfield, 6.14 ppm, while the corresponding signal for Tzse is found at a low field, 8.79 ppm. The mesomeric effect of the two α nitrogen atoms seems to have caused an upfield shift of the NH resonance in Etu. This may be due to enhanced neighbour anisotropy caused by the predominant contribution from the dipolar forms (b) and (c).

The ^{13}C NMR chemical shifts can be empirically correlated with the charge density on a given carbon atom in a molecule.[24-26] This is of interest in the study of the chemical reactivity of a molecule. The ^{13}C chemical shift arising from carbonyl carbon is found at 160.8 ppm and from thiocarbonyl carbons between 185.0 and 202.0 ppm. There is approximately a linearly relationship between ^{13}C chemical shifts and the calculated charge densities on thiocarbonyl carbon. Strict linearity is not expected since α-endo heteroatoms also vary. The ^{13}C resonance shifts downfield in the order Etu, Oxt and Tzdt and interestingly parallels the increasing bond order of the C=S grouping. Consistent with this observation, the ^{13}C resonance of selenocarbonyl carbon of Tzse occurs upfield (192.5 ppm) compared to that of the corre-

TABLE II

^{1}H and ^{13}C chemical shifts for some substituted azolidines

Compound†	^{1}H chemical shift (δ‡) N—H	(Z)CH_2	(N)CH_2	Compound	^{13}C chemical shift (δ‡) C=X	(N)CH_2	(Z)CH_2
		4.49	3.68				
Oxo	6.27	4.46	3.65	Oxo	160.8	40.8	65.0
		4.43	3.62				
Etu	6.14	—	3.78	Etu	185.2	45.4	—
		4.78	3.90				
Oxt	8.23	4.74	3.86	Oxt	190.6	44.2	70.4
		4.71	3.83				
		3.61	4.04				
Tzdt	8.50	3.58	4.01	Tzdt	202.0	51.4	33.8
		3.55	3.98				
		3.56	3.99				
Tzse	8.79	3.53	3.96	Tzse	192.5	53.5	34.8
		3.50	3.93				

† Etu in C_2D_5OD and rest in $CDCl_3$ as solvent.
‡ δ in ppm from internal TMS.

sponding thiocarbonyl carbon of Tzdt (202.03 ppm). Considering the electron releasing tendency of atom Z, it may be predicted that this tendency is in the order, N>O>S demonstrating that the contribution of the dipolar forms (b) and (c) increases from Tzdt<Oxt<Etu.

In conclusion, the present series of molecules show a reasonable correlation of the computed charge densities and bond orders within the framework of the CNDO/2 method with vibrational and NMR spectroscopic data.

EXPERIMENTAL

The compounds were synthesized as reported previously.[7-11] The ^{1}H NMR spectra were measured on a Bruker WH 270 MHz spectrometer in perdeuterated ethanol for Etu and in $CDCl_3$ for the remaining compounds using TMS as internal reference. ^{13}C NMR spectra were obtained using the same instrument operating at 67.89 MHz at 20° in Fourier transform mode under conditions of complete proton-noise decoupled as well as off-resonance decoupled mode. The samples were dissolved in suitable solvents as above and containing 2% TMS.

COMPUTATIONS

The calculations were carried out on a DEC 1090 computer. SCF MO calculations were performed within the frame work of the all valence electron CNDO/2 approximation with Pople's original parametrization.[17] A full basis set of orbitals was used including the 3d orbitals of sulfur. The geometry of Oxo, Tzdt and Etu were transferred from the results of X-ray diffraction studies.[18-20] The molecular parameters of Oxt were transferred from Oxo with the C=S bond length value assumed the same as in Tzdt. The calculations were not made for Tzse since the program was limited to the second row elements.

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