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Electronic Structure of the 1,5-Dithia-2,4,6,8-tetrazocine Ring. *Ab initio* and CNDO-CI Study

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The electronic and molecular structure of electron-rich S–N inorganic rings of the type $X(NSN)_2X$ are sensitive to the nature of X [1]. This is best exemplified by the structures of 3,7-biphenyl-(Ph_2–DTTA) and 3,7-bis(dimethylamino)-1,5-dithia-2,4,6,8-tetrazocine $[N(CH_3)_2]_2$–DTTA compounds, which may be related to the S_4N_4 ring by formally substituting two opposite sulfur atoms with C–Ph and C–$N(CH_3)_2$ groups, respectively. In the solid the former compound adopts a planar configuration, while the latter has a puckered structure [2]. The conformational problem of such molecules is very attractive and just recently an *ab initio* theoretical study employing minimal STO-3G basis sets has been reported [3]. However, in view of the importance of these systems in connection with the electronic and molecular structure of cyclic S–N compounds, we performed *ab initio* calculations on 3,7-dihydro-1,5-dithia-2,4,6,8-tetrazocine, H_2–DTTA, and on the corresponding diamino compound $(NH_2)_2$-DTTA, Fig. 1, by using different basis sets (minimal and valence-split) with and without inclusion of sulfur 3*d* polarization functions. In fact the important role of S_{3d} functions in describing the electronic structure of S–N compounds was noted previously [4]. Semi-empirical CI calculations were also carried out in order to investigate the nature and conformational dependence of the UV-visible electronic transitions of the studied compounds.

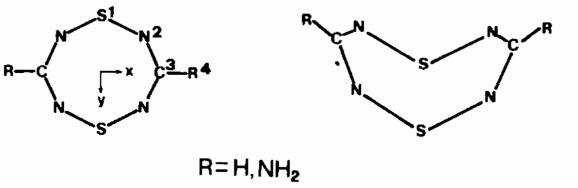

Fig. 1. Schematic structures of the planar and bent forms of DTTA ring.

Computational Method

Ab initio calculations were performed with the HONDO [5] and GAUSSIAN 80 [6] programs using STO-3G, STO-3G +5*d*, 4-31G and 4-31G + 5*d* basis sets (exponent of S_{3d} function 0.45). CNDO-CI calculations were carried out with the CNDO-SHIFT/UV program [7] by taking into account the lowest 30 monoexcited configurations. S_{3d} orbitals were included in the computations, their absence leading to unsatisfactory results. Two-centre Coulomb integrals were calculated by Nishimoto-Mataga formulae [8]. The geometries of the planar and folded DTTA ring are the experimental ones [2] slightly idealized to give D_{2h} and C_{2v} symmetries, respectively. The $-N(CH_3)_2$ group was replaced by NH_2 preserving the experimental C_3–N_4 distance.

Results

Total and relative energies of the studied structures are reported in Table I. A remarkable basis-set dependence of the relative stabilities of the conformers is evident. At the STO-3G level the planar and bent forms of H_2–DTTA have nearly the same energy, while the bent form of $(NH_2)_2$–DTTA is favoured over the planar one by 23 kcal/mol, consis-

TABLE I. Total (a.u.) and Relative (kcal/mol) Energies of 3,7-dihydro-1,5-dithia-2,4,6,8-tetrazocine, H_2–DTTA, and 3,7-bis-(diamino)-1,5-dithia-2,4,6,8-tetrazocine $(NH_2)_2$–DTTA.

Basis set	H_2–DTTA (D_{2h})	H_2–DTTA (C_{2v})	$(NH_2)_2$–DTTA (D_{2h})	$(NH_2)_2$–DTTA (C_{2v})
STO-3G	–1076.99572	–1076.99285	–1185.58989	–1185.62680
	0.0	1.8	23.1	0
STO-3G + 5*d*	–1077.27755	–1077.25729	–1185.87519	–1185.90111
	0.0	12.7	16.2	0.0
4-31G	–1088.07477	–1088.00156	–1197.94898	–1197.92286
	0.0	45.8	0.0	16.3
4-31G + 5*d*	–1088.24941	–1088.18882	–1198.12032	–1198.10869
	0.0	38.0	0.0	7.0

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TABLE II. Mulliken Population Analysis of 3,7-dihydro-1,5-dithia-2,4,6,8-tetrazocine, H_2–DTTA, and 3,7-bis(diamino)-1,5-dithia-2,4,6,8-tetrazocine, $(NH_2)_2$–DTTA: 4-31G + 5*d* Results.

	$S_1–N_2$	$N_2–C_3$	$C_3–N_4$	S–S	S_1	N_2	C_3	N_4
H_2–DTTA (D_{2h})	0.654	0.734		0.0	15.558	7.536	5.553	
	π (0.204)	(0.260)			(3.528)	(1.258)	(0.956)	
H_2–DTTA (C_{2v})	0.542	0.770		0.274	15.631	7.521	5.531	
NH_2–DTTA (D_{2h})	0.680	0.790	0.536	0.0	15.572	7.597	5.096	7.761
	π (0.180)	(0.256)	(0.010)		(3.555)	(1.336)	(0.921)	(1.852)
NH_2–DTTA (C_{2v})	0.632	0.780	0.474	0.258	15.635	7.563	5.117	7.772

tent with the experimental findings in the crystal [2] and with the STO-3G results of Boutique *et al.* [3]. The addition of S_{3d} functions to the minimal basis set significantly lowers the energy of the planar forms. The extended basis set (4-31G) further favours the planar structure of H_2–DTTA and reverses the order of stability of the $(NH_2)_2$-DTTA conformers; on the contrary, the role of the S_{3d} functions (4-31G + 5*d*) is now inverted, since they favour the bent structures.

The body of the above results clearly suggests that a further extension of the basis set is desirable, nevertheless at the present level of accuracy H_2–DTTA is quite safely a planar compound, whereas the D_{2h} and C_{2v} forms of (NH_2)–DTTA are not very different in energy and a finely balanced equilibrium could be possible.

The calculated (4-31G + 5*d*) charge densities and overlap populations are reported in Table II. Interestingly, the charge on the S atoms is nearly insensitive to the conformation and to the substituent (NH_2). This can be traced back to a balance in the σ, π electron migration involving the S atoms. In fact, on passing from the planar to the non-planar conformation the π contribution to the S–N bond lowers, while a trans-anular S–S bond is made mostly at the expense of the S–N bonds (Table II). A similar situation was found in $S_4N_4^{++}$ [1e]. Furthermore the S–S overlap populations in the C_{2v} conformations of both compounds are nearly equal. The structural effects of the NH_2 group seem to be subtly related to its electron donor-acceptor character with respect to the ring. In the planar (NH_2)–DTTA each NH_2 group donates to the ring 0.148 π-electrons and acquires 0.287 σ-electrons. The net balance gives rise to a positively charged ring (+0.278 e^-). This behaviour represents a noticeable difference with respect to the STO-3G results, which predict nearly zero net charge on the ring. The NH_2-π donation is destabilizing for the planar conformation at it induces a greater electron delocalization within the ring which reduces the S–N π overlap, owing to the π* character of the HOMO (*vide infra*). NH_2-σ effects the strength of the S–N–C σ network and increases the positive charge at C_3 (Table II). The latter effect may be considered stabilizing for the planar form. In fact, by extending the qualitative π model of $X(NSN)_2X$ by Chivers *et al.* [1c], the planar conformation should be favoured as the electronegativity of C_3 increases (see also [9]).

The approximate correlations between the outermost valence orbitals of planar and non-planar conformations of NH_2–DTTA are shown in Fig. 2. They provide useful information on bonding changes on passing from the D_{2h} to the C_{2v} structure. The unsubstituted $C_2S_2N_4$ ring is a planar 10 π electron system. The π orbitals are those expected from the interaction of two N–S–N allyl-type fragments perturbed by the interaction with the C_{2p_z} orbital. The $2b_{1u}$ HOMO (9.1 eV) has π* character being the antibonding S–N interactions (overlap population S–N = –0.06), only partially offset by bonding C–N interactions (o.p. C–N = 0.056). On passing from the planar to the non-planar conformation the $1b_{3g}$ and $1b_{1u}$ orbitals are noticeably destabilized, being delocalized over the S–N–C system. Destabilization is much less pronounced for $1b_{2g}$ and $1a_u$ orbitals which have nodes at the S atoms. The $2b_{1u}$ HOMO transforms into the more stable, strongly S–S bonding $7a_1$ σ orbital (o.p. S–S = 0.270), as was also described in the case of S_4N_4 [1e, 1f, 10]. It is interesting to note the evolution of the σ-type MOs. Particularly significant is the stabilization of the 5ag σ* orbital (o.p. S–N = –0.084, o.p. $C–N_2$ = –0.022) which transforms into the $3a_1$ S–S bonding orbital (o.p. S–S = 0.210). The MOs which may be considered as essentially arising from the N σ-lone-pair combinations ($3b_{1g}$, $4b_{3u}$, $4b_{2u}$ and $4a_g$) are all stabilized, except $3b_{1g}$, in the non-planar conformation where they lose some of the antibonding S–N or $C–N_2$ character.

Introduction of NH_2 groups in the 3,7 positions leads to a strong destabilization of the π* $3b_{1u}$ HOMO, computed at 7.0 eV. The HOMO–LUMO energy gap in the planar conformation is now much smaller than in the corresponding folded conformation and a stabilization of this form is expected. The conversion of the $3b_{1u}$ orbital into the $9a_1$ S–S bonding orbital (o.p. S–S = 0.282) (Fig. 2) is accom-

TABLE III. Electronic Spectrum of 3,7-bis(diamino)-1,5-dithia-2,4,6,8-tetrazocine: CNDO-CI Results.

Planar form (D_{2h})			Non-planar form (C_{2v})		
Frequency (nm)	Oscillator strength	Composition (transition)	Frequency (nm)	Oscillator strength	Composition (transition)
413	0.27	$0.93(3b_{1u}, 2b_{3g})$	322	0.00_6	$1.00(6b_2, 7b_2)$
302	0.51	$0.96(1a_u, 2b_{3g})$	259	0.03	$0.77(5a_2, 8b_1)$ $0.47(9a_1, 7b_2)$
233	1.08	$0.96(3b_{1u}, 3b_{2g})$	246	0.11	$1.00(4a_2, 7b_2)$
200	1.01	$0.89(1a_u, 2b_{3g})$	214	0.03	$0.69(8a_1, 7b_2)$ $0.60(9a_1, 7b_2)$
			214	0.05	$0.97(5b_2, 7b_2)$

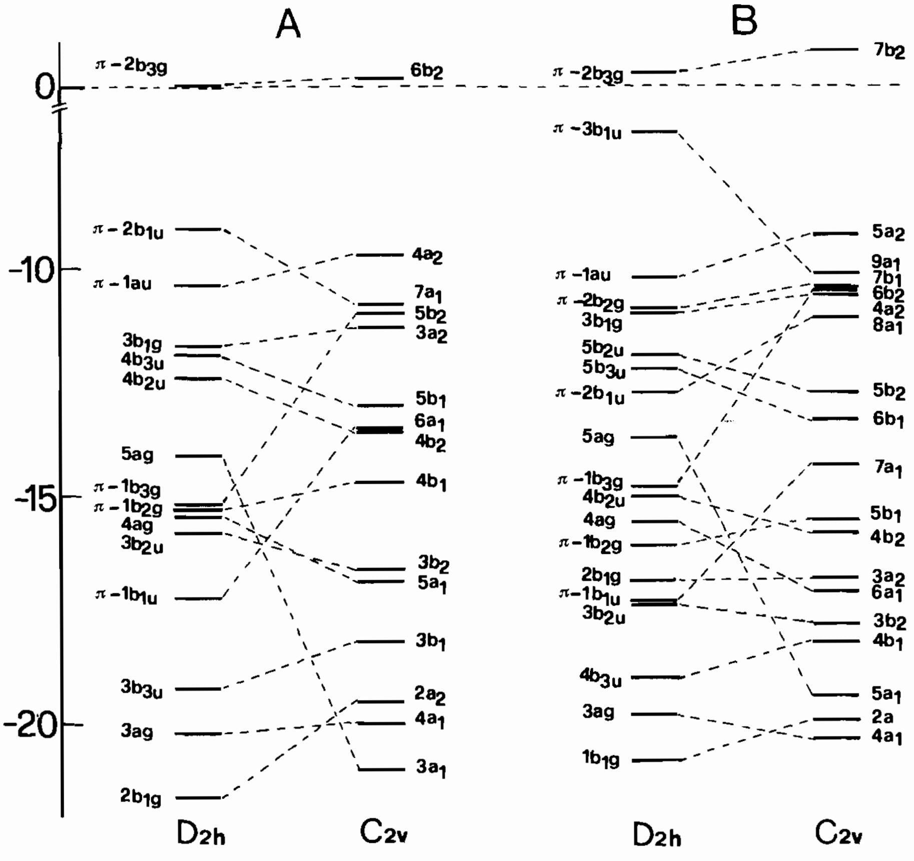

Fig. 2. Correlation diagram between the outermost valence energy levels of the planar (D_{2h}) and non-planar (C_{2v}) forms of 3,7-dihydro-1,5-dithia-2,4,6,7-tetrazocine (A) and 3,7-bis(diamino)-1,5-dithia-2,4,6,8-tetrazocine (B). Core orbitals are omitted in the notations.

panied by a 3 eV energy gain compared with the 1.7 eV figure for the corresponding process in H_2–DTTA. Note that the antibonding character of the HOMO in the S–N (o.p. S–N = –0.10) and C–N_4 bonds (o.p. C–N = +0.198) characterizes the nature of the latter bond, which shows no net π overlap (Table II). The HOMO in the C_{2v} form of $(NH_2)_2$–DTTA is the σ-type $5a_2$ orbital. It lies at considerably lower energy (9.3 eV) than the $3b_{1u}$ orbital in the D_{2h} conformation. The predicted high $3b_{1u}$ – $5a_2$ energy difference (*ca.* 2.3 eV) should provide a very favourable basis to probe the conformational behaviour of $(NH_2)_2$–DTTA in the vapour by means of UV photoelectron spectroscopy.

Electronic Spectrum of $(NH_2)_2$*–DTTA*

The lowest excited states of the planar and non-planar forms of $(NH_2)_2$–DTTA, as computed by the

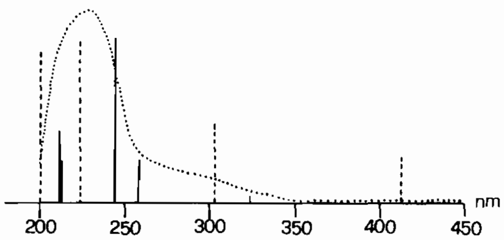

Fig. 3. Theoretical (CNDO-CI) spectrum of planar (dotted bars) and non-planar (full bars) forms of 3,7-bis(diamino)-1,5-dithia-2,4,6,8-tetrazocine. (·······): experimental spectrum of 3,7-bis(dimethylamino)1,5-dithia-2,4,6,8-tetrazocine [2].

CNDO-CI method, are shown in Table III and are compared with the experimental spectrum [2] in Fig. 3. It is worth noting that the character and sequence of the frontier MOs (HOMO, HOMO-1, LUMO, LUMO + 1) predicted by the CNDO-CI method are the same as in the *ab initio* 4-31G + 5*d* calculations. Some inversion occurs only in the crowded $9a_1$, $7b_1$, $6b_2$ and $4a_2$ orbitals. The theoretical spectrum of the planar $(NH_2)_2$-DTTA indicates absorptions at 413 and 302 nm, which arise from HOMO–LUMO and HOMO-1–LUMO π-type electronic transitions, respectively. Indeed it is remarkable that the corresponding Ph_2–DTTA, which is a planar compound [2], shows a low-energy absorption at 409 nm and intense absorptions in the range 250–350 nm with a maximum at 294.5 nm. On passing to the non-planar conformation no low-energy electronic transitions are predicted for $(NH_2)_2$–DTTA. This is in agreement with the transformation of the $3b_{1u}$ orbital into the more stable $9a_1$ orbital, so that the $3b_{1u} \rightarrow 2b_{3g}$ transition in the planar compound is replaced by the higher-energy $9a_1 \rightarrow 7b_2$ transition.

The $6b_2 \rightarrow 7b_2$ transition gives rise to an n-π^* state, which determines a charge transfer from the N_{endo} atoms to the S atoms. The agreement between the theoretical (C_{2v}) and experimental spectrum [2] may be considered as evidence of a non-planar conformation of $[N(CH_3)]_2$–DTTA in 96% ethanol [2]. However, here again solvent effects on the possible planar–non-planar equilibrium are possible, particularly because it is known that polar solvents tend to stabilize polar conformations.

Conclusions

The present results have shown that the calculated relative stabilities of the dithiatetrazocine ring are greatly dependent on the employed basis set. The unsubstituted H_2–$C_2S_2N_4$ ring is very probably a planar system. At 4-31G + 5*d* level of calculations the planar form of $(NH_2)_2$–DTTA is still favoured over the folded conformation, reversing the STO-3G results which strongly favour the non-planar structure. A very fine equilibrium between the two forms may be conceived in the vapour, so that solid state effects and solute–solvent interactions could well be important factors in determining the conformational preference in condensed media. The trend of the eigenvalue spectra and a Mulliken-type analysis of the individual MOs show the important role of the σ network rearrangement on passing from the planar to the non-planar form. A peculiar feature of these two structures is related to the high energy difference between the relative HOMOs and to the conversion of the π^* HOMO of the planar conformation into a more stable σ-type transanular S–S bonding orbital in the non-planar conformation. These features are reflected in the calculated UV-visible spectrum of $(NH_2)_2$–DTTA, which supports a non-planar structure of $[N(CH_3)_2]_2$–DTTA in ethanol solution. They also indicate that the gas-phase UV photoelectron spectrum of this compound would be very useful in order to probe the molecular conformation of the free molecule.

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