A Non-planar Excited State of 1,2,5-Thiadiazole

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Summary The vapour-phase u.v. absorption spectrum of 1,2,5-thiadiazole near 2600 Å has been shown to be $\pi \rightarrow \pi^*$ in nature and to involve a planar ground state and a non-planar excited state having a barrier to inversion of *ca.* 461 cm^{-1}.

IN its ground electronic state, 1,2,5-thiadiazole ($C_2H_2N_2S$) has been well characterized by a number of spectroscopic studies, and in particular, it has been shown to be a planar cyclic molecule of C_{2v} symmetry.[1] We report here the results of a u.v. spectroscopic study which shows that $C_2H_2N_2S$ has an excited electronic state which is non-planar and has a relatively low barrier to inversion. This appears to be the first reported observation of a cyclic molecule having a planar ground state and a non-planar excited state.

The u.v. absorption spectrum of $C_2H_2N_2S$ in the vapour phase extends from about 2800 to 2500 Å. Comparison of spectra of the vapour at *ca.* 25 °C with those of the vapour at *ca.* −60 °C shows that the origin band of the electronic transition is at 37,935 and 37,983 cm^{-1} for $C_2H_2N_2S$ and $C_2D_2N_2S$, respectively. Three fundamental vibrations can be used to explain almost all the observed vibronic bands. Two of these are totally symmetric, namely ν_4, the CH symmetric in-plane bend, and ν_5, a symmetric ring in-plane bend.[2] ν_5 has been observed in progressions of three quanta in the ground and excited states, while ν_4 has been observed only in single quanta. The values observed for these fundamentals in the ground and excited states are summarized in Table 1.

The third fundamental vibration observed in the spectrum is the non-totally symmetric vibration ν_{15}, a ring out-of-plane bending mode of B_1 symmetry. The observed values of ν_{15}'' for $C_2H_2N_2S$ and $C_2D_2N_2S$ are 520 and 506 cm^{-1} from the i.r. and Raman and 520 and 510 cm^{-1} from the u.v. The vibrational energy levels of ν_{15} in the excited state are listed in Table 2. These levels have been fitted to a double-minimum potential function of the type $V(Q) = 1/2\lambda Q^2 + A\exp(-a^2Q^2)$ using the tables of eigenvalues published by Coon, Naugle, and McKenzie.[3] A comparison of the observed and calculated energy levels and a summary of the potential function parameters used are given in Table 2.

TABLE 1

Observed ground and excited state fundamental vibrational frequencies

	Ground State[a]	Excited State
	$C_2H_2N_2S$	
ν_4	1041 (1041)	990
ν_5	805 (806)	604
	$C_2D_2N_2S$	
ν_4	851 (849)	649
ν_5	754 (753)	610

[a] Values in parentheses from i.r. and Raman.[2]

TABLE 2

Observed and calculated energy levels for ν_{15}' and potential function parameters

	$C_2H_2N_2S$		$C_2D_2N_2S$	
ν_{15}'	Obs.	Calc.	Obs.	Calc.
0	0·0	0·0	0·0	0·0
1	0·6	1·0	<1	0·6
2	226·2	226·8	232·3	230·7
3	248·8	248·7	247·4	245·6
4	400·5	401·1	403·1	404·2
5	492·9	493·5	485·2	483·5
6	627·1	626·6	606·0	613·2
$G(0)$	—	127·8	—	127·2
ρ	1·20		1·20	
ν_0	174·0		172·2	
B	2·649		2·858	
Barrier	460·8		492·1	

The barrier to inversion is calculated to be 461 and 492 cm^{-1} for $C_2H_2N_2S$ and $C_2D_2N_2S$, respectively. The value of

461 cm^{-1} obtained for the inversion barrier of $C_2H_2N_2S$ is a more reliable estimate of the true barrier since the measurements for $C_2H_2N_2S$ were made from high resolution spectra and so are more accurate than those for $C_2D_2N_2S$.

Almost all the observed bands are of the same type and show a relatively narrow maximum at shorter wavelength separated by *ca.* 14 cm^{-1} from, and having a relative intensity of *ca.* 1·3 times that of, a broader maximum at longer wavelength. Using the known ground state rotational constants[1] and reasonable values for the excited state rotational constants in an asymmetric rotor band contour program it has been possible to calculate contours resembling those obtained experimentally only for type A selection rules. This means that the electronic transition is $^1A_1 \leftarrow {}^1A_1$, and from simple MO considerations, this indicates that the transition is $\pi \rightarrow \pi^*$ in nature. This assignment is supported by the wavelength and intensity of the absorption and the effects of changing solvent polarity.[4]

In its ground electronic state, $C_2H_2N_2S$ has been shown to have considerable aromatic character, presumably as the result of sulphur atom *p* and *d* orbital participation as *pd* hybrids in the π bonding of the ring.[4] The data presented here show clearly that promotion of an electron from a π to a π^* orbital destroys the aromatic π bonding in $C_2H_2N_2S$ and so may be useful in theoretical studies of π bonding in sulphur containing molecules.

We thank the National Research Council of Canada for financial support.

(*Received, August 24th,* 1971; *Com.* 1487.)

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