Microwave Spectrum and Conformation of Glycine

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Summary The microwave spectrum of glycine vapour has been measured and analysed; it is in the molecular form with a dipole moment of 4·5—4·6 D and probably having conformation (4), which is in conflict with a recent theoretical study that implies that conformation (3) is more stable.

BECAUSE of its pivotal biological significance as the simplest amino acid there is considerable interest in the structure and other properties of the glycine molecule. Although X-ray and neutron diffraction studies of the glycine crystal have been reported[1] revealing bond lengths, angles, and packing arrangements in the crystal, it is of great importance to have information about an isolated glycine molecule. This would make solid-state effects apparent, not only in relation to intermolecular hydrogen bonding but also because glycine exists as the zwitterion in the solid state, whereas it is expected that it might be in the less polar molecular form when isolated as a gaseous molecule. However the study of the rotational spectrum of glycine vapour has presented considerable difficulties because of the relatively low volatility coupled with its thermal instability. In the last few years there has been a further stimulus to endeavouring to study the rotational spectrum of the molecule because of the possibility of detecting interstellar glycine.

TABLE 1. Some of the measured microwave transition (MHz) attributed to glycine

$7_{16} \leftarrow 6_{15}$	51027.4	$4_{22} \leftarrow 3_{21}$	29398.6
$8_{17} \leftarrow 7_{16}$	57341.0	$4_{23} \leftarrow 3_{22}$	28215.6
$8_{18} \leftarrow 7_{17}$	60757.3	$8_{35} \rightarrow 7_{34}$	59137.0

We have now succeeded in detecting the microwave spectrum of glycine in a specially constructed cell designed to maintain it at a temperature at which it has an appreciable vapour pressure (160—200 °C) while minimising effects of decomposition. It consisted of a large, uniformly heated, stainless steel vacuum tank fitted with parallel plates to conduct the microwaves through the vapour and to enable Stark-modulation of signals to be employed.

More than 200 lines attributable to glycine have been measured in the frequency range 35—63 GHz. It proved possible to assign many of the lines as a-type transitions in the spectrum of an almost rigid rotor with the following values of the spectral parameters: $A = 10129·200$, $B = 4071·449$, $C = 3007·511$, $D_J = 0·00052$, and $D_{JK} = 0·00548$ MHz. The frequencies of some of the assigned lines are given in Table 1. In addition, by measuring the Stark effect on the $4_{23} \leftarrow 3_{22}$ transition we have obtained a value of 4·5 D (1·3 × 10^{-29} C m) for the component of the molecular dipole moment along the a inertial axis. We were unable to detect any b-type transitions and estimate that $\mu_b < 1$ D. Thus the molecular dipole moment is 4·5—4·6 D.

While we cannot deduce the molecular geometry from just the set of rotational constants for a single isotopic species of glycine, we can compare our results with values of the constants calculated for various plausible conformations

(1)   (2)   (3)   (4)   (5)   (6)
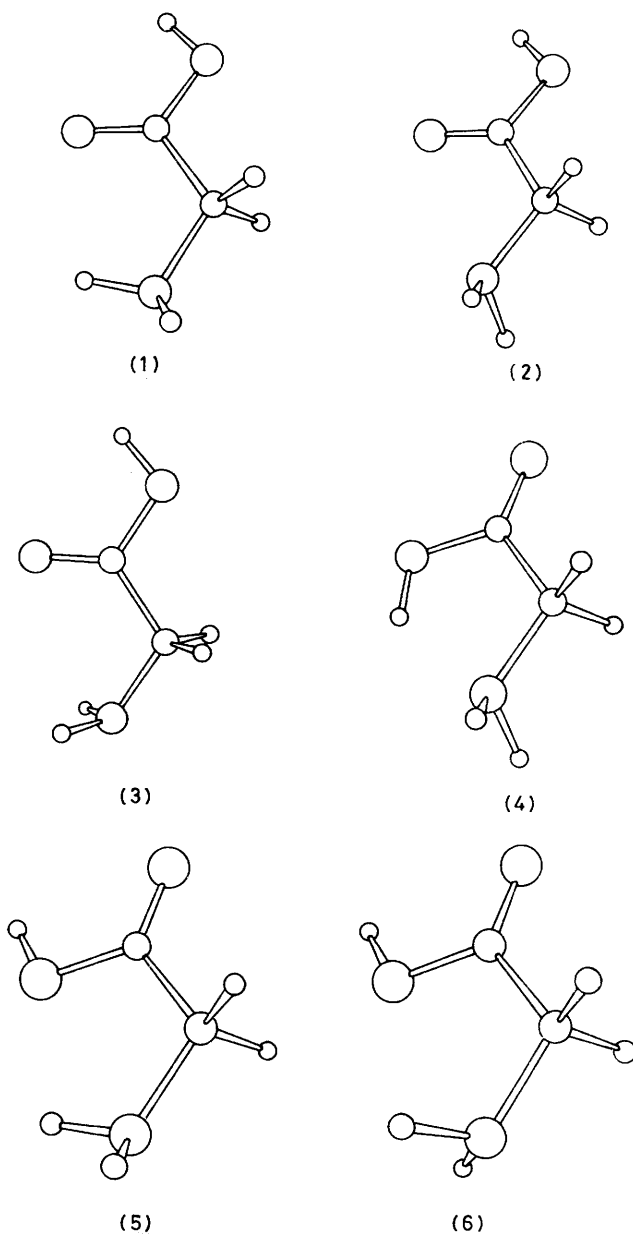
FIGURE

of the molecule. The various conformations are shown in the Figure and the predicted rotational constants and dipole moment components are listed in Table 2. Geometries were estimated by combining data for propionic acid[2] and methylamine.[3] The dipole components were computed by using the simple but reasonably reliable assumption that dipole moments can be predominantly attributed to lone pair electrons and using the values of 1·70, 2·35, and 1·31 D for the hydroxy oxygen, carbonyl oxygen, and amino

nitrogen, respectively. We did not seriously consider zwitterion structures because they would imply very much greater values of the dipole moment than that observed.

TABLE 2. Rotational constants and dipole moment components of glycine conformations

Confor-mation	A^a	B^a	C^a	$\mu_a{}^b$	$\mu_b{}^b$	$\mu_c{}^b$
(1)	10·45	3·88	2·91	0·3	0·1	1·1
(2)	10·06	3·76	2·87	0·2	1·9	0·0
(3)	10·36	3·90	2·93	1·0	0·2	0·0
(4)	10·47	4·03	3·01	3·5	1·7	0·0
(5)	10·21	4·12	3·02	0·1	0·6	1·1
(6)	10·11	4·15	3·05	0·6	0·8	0·0
Exp. values	10·13	4·07	3·01	4·5	≤1·0	0·0

[a] In GHz. [b] In D.

Uncertainties in the predicted rotational constants are too great to enable a reliable choice to be made from them alone but the predicted dipole components of conformation (4) are most in harmony with our observations. Moreover for this conformation alone one expects some of the rotational transitions to be readily modulated at very low voltages. It was this observation that helped in the initial stages of the assignment of the spectrum. An alternative configuration (3) has been predicted to be more stable than (4) on the basis of restricted Hartree–Fock M.O. calculations[4] but (3) is predicted by us to have too low a value of the dipole moment components to be compatible with our assigned spectrum. We have not so far identified any lines than can be attributed to this conformer of glycine. We would expect such lines to be weaker if present at all. However, it is possible that the vapour contains one or more of the other conformers whose lines have so far escaped detection because they are less intense and less easily moderated by the Stark fields attainable in our spectrometer.

We conclude that the most likely conformation of the glycine molecule in the vapour state is (4).

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[2] O. L. Stiefvater, J. Chem. Phys., 1975, 62, 233.
[3] D. R. Lide, J. Chem. Phys., 1957, 27, 343.
[4] S. Vishveshwara and J. A. Pople, J. Amer. Chem. Soc., 1977, 99, 2422.