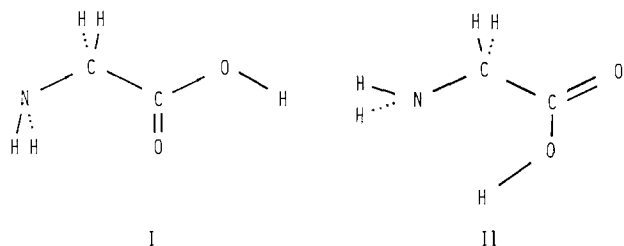


Investigations Concerning the Apparent Contradiction between the Microwave Structure and the *ab Initio* Calculations of Glycine

Sir:

Because of the current search for glycine in interstellar space, its un-ionized structure and microwave spectrum^{1,2} are of particular interest. The microwave spectrum of glycine was recently recorded independently by two different groups.^{1,2} Both found evidence for the presence of conformation II; they did not find evidence for the presence of conformation I in the vapors of this compound. This result is in some contrast to a



previous conformational analysis of glycine³ which was based on quantum mechanical energy calculations using standard restricted Hartree-Fock molecular orbital theory with the 4-31G basis.⁴ Structure I was found in this study as the minimum energy conformation. A second local energy minimum, II, was found 2.2 kcal/mol above I. Standard values for bond lengths and angles were used in these calculations.

We have now performed a complete geometry optimization of the structures I and II in order to be able to comment on this apparent contradiction between an observation and a generally accepted model of reality. Our calculations suggest that I is indeed the conformational ground state of glycine; that differences in zero-point energies may reduce its total energy difference relative to II; and that it has a much smaller dipole moment than II. Glycine vapors at thermal equilibrium might, therefore, very well exist as a conformational mixture containing several conformers, the most stable one of which would not produce the strongest microwave signals.^{1,2} The approximate equilibrium geometries reported in this communication are also interesting in view of the general importance of this system. Our geometry for II was found to reproduce the experimental data like a refined structure.²

Our *ab initio* calculations employed the FORCE method by Pulay.⁵ Program TEXAS was used^{6,7} with a 4-21G basis set.⁷ This basis is more economical than the 4-31G basis;⁴ yet it produces results which are very similar and in good agreement with experiment.^{7,8} The geometrical parameters listed in Table I were generated by ~15 iterations (in each case) using the variable metric minimization scheme.^{9,10} Each iteration required ~4-5 h of CPU time on our IBM 370/155.

The energy difference between I and II after complete optimization is the same (2.2 kcal/mol, Table I) as the one reported in ref 3 for the standard geometry conformers. The figure of Table I is more reliable, however, than the energy difference between the unrelaxed geometries.³ In a similar study of dimethylhydrazine,¹¹ for example, we have found that the relative energies of different conformers can vary significantly when their bond lengths and angles are optimized. Indeed, the optimized geometrical parameters of I and II are significantly different (Table I).

We have also calculated the zero-point vibrational energies of I and II using the normal coordinate program by Sellers et al.^{12,13} The force constants used were very approximate. Bond stretching constants for the skeleton of I were obtained from 4-21G calculations. Average force constants for angle deformations were transferred from smaller and related molecules.¹⁴ The calculations yielded a zero-point energy for I which was

Table I. 4-21G *ab Initio* Optimized Structural Parameters of Glycine^a

	I	II
$r(\text{N—H})$	1.001	1.000
$r(\text{N—C})$	1.457	1.474
$r(\text{C—H})$	1.081	1.081
$r(\text{C—C})$	1.514	1.535
$r(\text{C=O})$	1.203	1.202
$r(\text{C—O})$	1.364	1.345
$r(\text{O—H})$	0.966	0.975
$\theta(\text{NCC})$	113.28	110.19
$\theta(\text{CC=O})$	126.41	122.32
$\theta(\text{CC—O})$	110.62	113.82
$\theta(\text{CO—H})$	112.28	108.44
$\theta(\text{CNH})$	113.27	114.49
$\theta(\text{CCH})$	107.87	107.67
$\theta(\text{HNH})$	110.29	111.36
$\theta(\text{HCH})$	107.04	107.37
$\theta(\text{NCH})$	110.27	111.87
$\tau(\text{NCC=O})$	0.0	180.0
$\tau(\text{NCCO})$	180.0	0.0
$\tau(\text{CCOH})$	180.0	0.0
$\tau(\text{CCNH})$	63.29	114.83
$\tau(\text{O—CCH})$	57.65	122.25
$E(\text{tot})$	-282.15805	-282.15460
$E(\text{rel})$	0.0	2.2
μ	1.10	6.54
$F(\text{res})$	<0.007 ^b	<0.004

^a Bond lengths, r , in Ångströms; bond angles, θ , torsional angles, τ , in degrees; total energies, $E(\text{tot})$, in au; relative energies, $E(\text{rel})$, in kilocalories/mole; dipole moments, μ , in debyes; largest residual force, $F(\text{res})$, in millidyne. ^b Only one force had this magnitude; all other forces in I were <0.005.

~1 kcal/mol higher than that of II. Because of the approximate nature of the force field applied, the magnitude of this figure is very uncertain at best. However, since the same constants were used in the analysis of both I and II, the comparison is qualitatively meaningful. It seems to indicate that the same factors which stabilize an equilibrium structure generate destabilizing zero-point energy contributions to its corresponding thermal average molecular conformation.

Because of our geometry optimization it is now also possible to compare the calculated dipole moments of I and II (Table I). Since the dipole moment of II is significantly larger than that of I, it should be favored over I in the observation of its microwave spectrum. The experimental value for the component of the molecular dipole moment of II along the a inertial axis was found to be¹ 4.5 D. This confirms that the total molecular dipole moment for II should be relatively large as the calculated value of 6.5 D (Table I) seems to suggest.

The *ab initio* model and the microwave spectrum of glycine need, therefore, not necessarily be contradictory. The energy difference calculated for I and II is small enough that, taking the inherent uncertainties into account, the vapors of glycine may very well exist in a conformational mixture containing I and II. Because of the factors influencing the intensities of microwave signals, conformation I might remain undetected in such a mixture;^{1,2} so, whereas there is no experimental evidence for the presence of I, it can not be ruled out definitely either. The possibility of a serious failure of the *ab initio* procedures on this level as well as other interpretations of the apparent discrepancy must, of course, also be kept in mind.

The potentially delusive effect of experimental observation is a particularly fascinating aspect of this case. The interactive application of theoretical and experimental procedures seems to be the most powerful presently available approach to understanding the conformational behavior of free molecules.^{15,16}

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Harrell L. Sellers, Lothar Schäfer*

Department of Chemistry, University of Arkansas
Fayetteville, Arkansas 72701

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Carbon-13 Nuclear Magnetic Resonance of *cis*- and *trans*-Polyacetylenes^{1a}

Sir:

Polyacetylene, (CH)_x, is the simplest conjugated organic covalent polymer in which the electrons from the unsaturated π system are expected to be delocalized along the polymer chains. However, because of the combined effects of bond alternation² and Coulomb correlation,³ there is an energy gap in the excitation spectrum leading to semiconducting behavior.⁴⁻⁷

Studies by Shirakawa et al.⁴⁻⁷ show that both the *cis* (A) and the *trans* (B) isomers can be synthesized in the form of silvery, flexible, crystalline films. Recent investigations show that both isomers may be doped with small quantities of electron-attracting species such as iodine, AsF₅,⁸⁻¹⁰ etc., or with electron

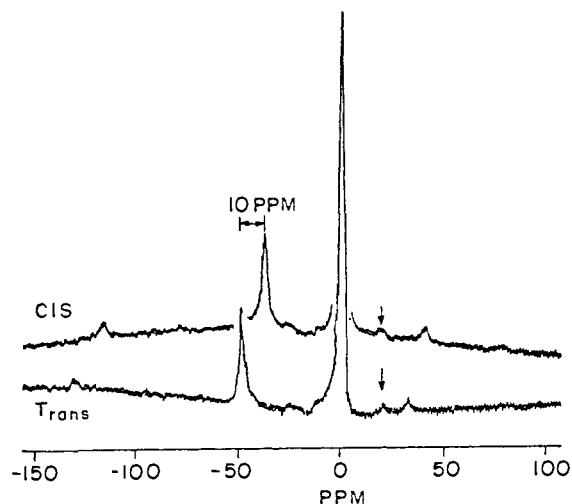
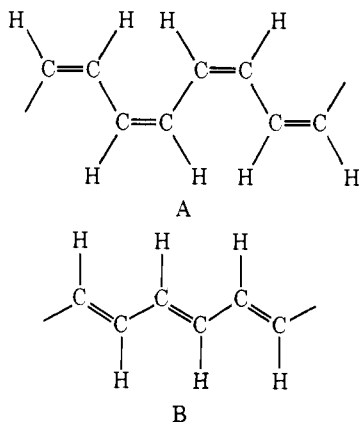


Figure 1. Natural abundance ¹³C spectra of *cis*- and *trans*-polyacetylenes, obtained in an external field of 39 T. Total averaging time was ~1 h to each ~0.5-g sample. Weak lines not mentioned in the text are spinning sidebands. To convert the Delrin-based shift scale to parts per million downfield from Me₄Si, subtract 90 ppm and change the sign.

donors such as sodium¹⁰ to give a series of semiconductors whose conductivity increases with dopant concentration. In the range of 1-3 mol % dopant concentration, the doped films undergo a semiconductor-metal transition to yield flexible films of "organic metals".^{9,10} The conductivity of some of these films are remarkably high, up to 10¹² times greater than the parent polymer. Thus polycrystalline films of [CH(AsF₅)_{0.14}]_x have a room temperature conductivity of 1.0 × 10³ Ω⁻¹ cm⁻¹. This is better than the best single crystals of TTF-TCNQ and related organic conductors.

Elemental analyses of both isomers correspond exactly to the empirical formula (CH)_x.⁶⁻⁸ Identification of the isomers has been made by vibrational spectroscopic studies of thin films.⁴ These data do not, however, show if some cross-linking had occurred by means of sp³-hybridized carbon during polymerization. The empirical formula would be unchanged even if some of the -CH= sp²-hybridized carbon atoms were in fact in the -CH< sp³-hybridized form. Bromination of the polymer to give (CHBr)_x resulted in only ~75% of the expected bromine uptake assuming that all carbons were sp² hybridized and that bromine added completely to all double bonds. The fact that the (CH)_x is insoluble in all solvents tested to date makes it impossible to carry out the bromination under homogeneous conditions which would tend to promote complete bromination. It was therefore not possible to determine whether or not the *cis* or *trans* isomers were "structurally pure". This was a particularly important matter since any interruption of the π system in the polymer by the presence of sp³-hybridized carbon atoms might be expected to affect significantly the electrical properties of the doped or undoped (CH)_x. In order to interpret the physical studies on these materials, it is of fundamental importance to have definitive information on the extent of cross-linking and the concentration of sp³-hybridized carbon.

Among experimental methods which might be applied in such studies, NMR offers a special advantage since chemical shifts are highly diagnostic of chemical structure, and should lend themselves to detection of chemical and stereochemical impurities which represent defects in the idealized *cis*- or *trans*-polyene chains.

Conventional NMR techniques are incapable of resolving shifts of the expected size except in liquids, whereas the properties which make (CH)_x interesting are characteristic of the ordered solid state. Accordingly we have used *cis*- and *trans*-(CH)_x to illustrate the usefulness of "modern" methods