pendent of sample composition. Since these splittings are unaffected by "slow" motions and are reduced by "rapid" motions, the observation is equivalent to the statement that no motion changes from the slow limit to the rapid limit as a function of sample composition. Second, T_{1B} and T_{1F} are also independent of sample composition. This result places a further restriction on the system that the correlation times for motions controlling relaxation in both bound and free sites are independent of sample composition.[6] Third, a nonzero splitting is obtained for the free site, and this is indicative of restricted motion.[7]

Interpretation of T_{1B} and T_{1F} values can be done only in terms of the specific motion controlling each relaxation; a procedure similar to that used for D_2O relaxation in lecithin/D_2O systems might be used.[8] Our interpretation of the quadrupole splittings (see below) suggests that there are several rapid motions that could contribute to spin–lattice relaxation in this system which will make interpretation of T_1 values difficult.

The magnitude of $\Delta\nu_B$ can be explained in a straightforward manner, using an approach similar to that used for aqueous lecithin phases.[9] If the binding site for EG is taken to be the phosphate group on L, then local rotation of EG while bound to L could result in the P–O bond axis becoming a symmetry axis. Rapid reorientation of L around an axis parallel to the long chain is also expected.[10,11] We assume tetrahedral geometry for EG and nonbonding orbitals on O, and an O–P–O bond angle[13] of 121.6°; from these values, assuming the motions above, we calculate a splitting of 2.0 kHz, which agrees with the $\Delta\nu_B$ value given in Table II.

This preliminary study indicates that the EG/L nonaqueous system lends itself to a more straightforward interpretation than does the H_2O/L system. This is due partly to the fact that in the aqueous system, solvation of the L head group apparently involves at least five water molecules.[9] We are continuing these studies by investigating other features of the nonaqueous lecithin liquid crystalline phase, including proton relaxation, translational diffusion, and the effect of varying the diol chain length.

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(6) Spin–lattice relaxation times are usually given in terms of spectral density functions, which are developed in terms of correlation times. See: A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, Oxford, 1961, Chapter 8.

(7) The concept of restricted motion has been discussed in C. H. A. Seiter and S. I. Chan, *J. Am. Chem. Soc.*, **95**, 7541 (1973).

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(9) K. Gawrisch, K. Arnold, T. Gottwald, G. Klose, and F. Volke, *Studia Biophys.*, **74**, 13 (1978).

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(11) Recent NMR studies (see ref 12) suggest that this rotation may be biased, which will make analysis of splittings more complex than that used herein.

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(13) The bond angle found in diethyl phosphate anion was used in the calculation; see: Y. Kyogoku and Y. Iitaka, *Acta Crystallogr.*, **21**, 49 (1966).

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Theory versus Experiment: The Case of Glycine

Sir:

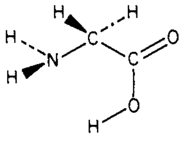
Some time ago, the microwave spectrum of glycine was recorded independently by Brown et al.[1] and by Suenram and Lovas.[2]

Table I. 4-21G ab Initio Optimized Structural Parameters of Glycine[a]

	I	II	III
r(N–H)	1.001	1.000	1.001
r(N–C)	1.457	1.474	1.457
r(C–H)	1.081	1.081	1.081
r(C–C)	1.514	1.535	1.522
r(C=O)	1.203	1.202	1.204
r(C–O)	1.364	1.345	1.365
r(O–H)	0.966	0.975	0.966
θ(NCC)	113.28	110.19	115.92
θ(CC=O)	126.41	122.32	125.42
θ(CC–O)	110.62	113.82	112.18
θ(CO–H)	112.28	108.44	111.49
θ(CNH)	113.27	114.49	112.58
θ(CCH)	107.87	107.67	107.14
θ(HNH)	110.29	111.36	109.79
θ(HCH)	107.04	107.37	106.61
θ(NCH)	110.27	111.87	109.80
τ(NCC=O)	0.0	180.0	180.0
τ(NCCO)	180.0	0.0	0.0
τ(CCOH)	180.0	0.0	180.0
τ(CCNH)	63.29	114.83	62.38
τ(O–CCH)	57.65	122.25	122.96
E(tot)	−282.15805	−282.15460	−282.15497
E(rel)	0.0	2.2	1.9
μ	1.10	6.54	1.76
F(res)	<0.007	<0.004	0.005

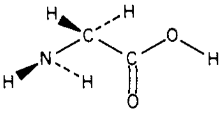
[a] Bond lengths, r, in Å; bond angles, θ, and torsional angles, τ, in deg; total energies, E(tot), in au; relative energies, E(rel) in kcal/mol; dipole moments, μ, in D; largest residual force, F(res), in mdyn. Pulay's FORCE program with the 4-21G basis[6] was used in connection with the normal coordinate force relaxation procedure of Sellers et al.[7] to generate the optimized parameters.

From the experimental evidence, both groups concluded that the particular conformer observed was II. Since no isotopic substitutions were performed, however, quantitative structural information regarding precise bond lengths and angles could not be obtained. In parallel with the microwave work, Sellers and Schäfer carried out a completely relaxed ab initio equilibrium structure on two low-energy forms of glycine.[3]



II

These calculations confirmed the results of earlier less sophisticated calculations[4] in that they predict II to be less stable than I by approximately 1–2 kcal/mol. The striking fact here,



I

however, is that the refined ab initio calculations for II yielded a structure that reproduced the microwave rotational constants with an amazing degree of accuracy. Although it is possible that the excellent agreement was simply fortuitous, it was also possible that the calculations were providing a reasonable estimate of the structure and relative energy. In view of this, two interpretations were possible. Brown et al.[1] concluded that II was "the most likely conformation of glycine in the vapor state", even though they could not exclude the possibility that the vapor contained one or more other, undetected species. Suenram and Lovas[2] and Sellers and Schäfer[3] concluded that the exclusive observation of II did not

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(3) Sellers, H. L.; Schäfer, L. *J. Am. Chem. Soc.* **1978**, *100*, 7728–7729.

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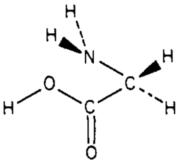
allow any inference regarding its energy relative to I. This is possible if II has a larger dipole moment than I, since intensities of transitions in the microwave region are proportional to the square of the dipole moment. As shown in Table I, this is most likely the case since the ratio of the squares of the calculated dipoles provides II with a considerable advantage in line intensity. The microwave spectrum of an equilibrium mixture of glycine could thus be dominated by the spectrum of the less populated conformer II. If this were the case, the apparent contradiction between the ab initio model and the experiment could be reconciled.

In view of this interesting situation, the millimeter wave work with glycine at the National Bureau of Standards was continued after the original results of the high-energy conformer (II) were published.[2] Spectral predictions based on the optimized geometry of I from the calculations of Sellers and Schäfer were used to help guide the search for a potentially existing second conformer of glycine with a more sensitive spectrometer. Indeed, a number of weak transitions were found close to the predicted values, and eventually an assignment was obtained which allowed the determination of the rotational constants for this conformer (Table II). A report on the experimental details and spectral analysis is in preparation.[5] The derived rotational constants are again in extremely good agreement with those predicted by the ab initio structure for conformer I (Table II). In order to provide additional evidence that the newly assigned species was indeed the lowest energy conformer, an additional unconstrained geometry optimization (4-21G basis) was carried out for conformer III (results in Table I) which was also predicted to be fairly low energy.[4] As can be seen in Table II, the observed rotational constants are in much closer agreement to those of I than III. In addition, the measured dipole moment and relative energies are also in very good agreement with the theoretical values for I. It thus appears that, at the present time, the existing information requires the identification of the newly assigned conformer as conformer I.



III

In a critical evaluation of this result, it must be kept in mind that the precise structural aspects of un-ionized glycine are still experimentally undetermined. So, whereas the conclusion presented above is reasonable, it is, by definition, also tentative. In order to clarify the choice of conformer I rather than III as the carrier of the new spectrum, an estimation of the uncertainties involved in the comparison of experimental versus theoretical rotational constants is warranted. There are two major sources of uncertainties which contribute to the differences between the observed rotational constants and those calculated from the theoretical structures (Table I). First, the accuracy of the theoretical structures must be considered. In order to assess the sensitivity of the rotational constants to variations in the structural parameters, we have calculated the average change in A, B, and C when all bond lengths and angles are changed by 1% of their theoretical values. This calculation results in ~0.2% change in A, B, and C for conformer I. Similar results are obtained for conformers II and III. Thus, structural changes of ~1–2% affect the rotational constants by ~0.2–0.4%.

Table II. Calculated and Observed Rotational Constants, Dipole Moments, and Relative Energies for Several Conformations of Glycine[a]

	expt	theory[b]	obsd − calcd[c]	% difference
		Gly-I[d]		
A	10341.69 (26)	10300.8	40.9	0.40
B	3876.198 (14)	3890.3	−14.1	−0.36
C	2912.362 (14)	2917.8	−5.4	−0.19
μ_a	1.00 (15)	1.0		
μ_b	>0[e]	0.5		
E(rel)	0	0		
		Gly-II[f]		
A	10130.47 (62)	10095.4	35.1	0.35
B	4071.473 (36)	4107.6	−36.1	−0.89
C	3007.538 (44)	3021.0	−13.5	−0.45
μ_a	4.5[g]	6.4		
μ_b		1.4		
E(rel)	490 (150)	770 [350][h]		
		Gly-II(ND_2CH_2COOD[d])		
A	9489.9 (6.3)	9436.4	53.5	0.56
B	3681.02 (27)	3713.3	−32.3	−0.88
C	2776.47 (32)	2790.6	−14.1	−0.51
		Gly-III		
A		9949.6	392.0[i]	3.8
B		4052.0	−175.8	−4.5
C		2976.6	−64.2	−2.2
μ_a		0.3		
μ_b		1.7		
E(rel)		665		

[a] The units are MHz for the rotational constants, D for the dipole moment components, and cm^{-1} for *E*(rel). The numbers in parentheses represent the uncertainties associated with the observed parameters. [b] The theoretical constants were obtained by using the geometrical parameters of Table I. [c] This column gives the difference between the experimental and theoretical rotational constants. [d] This work, a detailed spectroscopic paper describing the microwave work on I, will be forthcoming in the near future.[5] [e] Four transitions have been observed which are consistent with μ_b dipole transitions, but no quantitative determination of μ_b has been made. [f] Experimental values from ref 2. [g] Value from ref 1. [h] Value in brackets is an estimate of the approximate difference in zero-point energy favoring II with respect to I. For details, see ref 3. [i] Obsd − calcd value if the weaker experimental species is assigned to conformer III.

A second source of uncertainty in this comparison lies in the fact that the theoretical structure represents a hypothetical equilibrium geometry (r_e) while the experimental data are obtained from the ground vibrational states (r_0). Since no comparisons between r_e and r_0 structures exist for molecules with more than three atoms, it is difficult to ascertain the size of this effect. Watson[8] has reported a detailed analysis of structure determination for several diatomic and triatomic species. The equilibrium and vibrational ground-state rotational constants employed in Watson's analysis show differences of approximately 0.5%. Similarly, Schwendeman[9] has examined this problem and discusses the structure of 2-chloropropane determined by several methods which approximate the equilibrium structure. Here again, the rotational constants differ by 0.3–0.7% from the observed values. Thus, our comparison of the theoretical (equilibrium) and observed (vibrational ground state) rotational constants in Table II should be expected to show differences on the order of 0.5% due to zero-point energy contributions.

From the above discussion, one expects to see total deviations between theoretical and experimental rotational constants for a given conformer of up to ~1%. This is encouraging since the obsd − calcd values for conformers I and II are all less than 1% whereas those for conformer III are in the 2–4% range. Hence, the assignment of the observed spectrum to I rather than III can be justified solely on the basis of the rotational constant agreement. The measured dipole moment and the fact that the newly assigned

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conformer is 490 ± 150 cm^{-1} lower in energy than II also support this conclusion.[5]

The results obtained here have a direct bearing on other studies. In particular, the higher energy form (II) of glycine has been sought unsuccessfully in interstellar molecular clouds.[10] Since the interstellar clouds are quite cool ($T < 100$ K), one anticipates that only the lowest energy states of a molecule will be populated. As a result, negative interstellar searches for conformer II may be much less significant than for conformer I.

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Molecular Structure of $Mo(CO)_2[S_2CN\text{-}i\text{-}Pr_2]_2$. A Trigonal-Prismatic Electron-Deficient Molybdenum(II) Carbonyl Derivative

Sir:

Molybdenum carbonyl derivatives of both Mo(0) and Mo(II) adhere to the effective atomic number rule with great regularity.[1] In view of the premise that 16-electron species are common intermediates for reactions involving these and related compounds,[2] the properties of molybdenum carbonyl compounds which are formally electron deficient are of fundamental importance. We report a single-crystal X-ray study of $Mo(CO)_2(S_2CN\text{-}i\text{-}Pr_2)_2$ (**1**),[3] a 6-coordinate molybdenum(II) dicarbonyl monomer.[4] Previous reactivity studies have identified related compounds as reversible carbon monoxide carriers[5] and explored their addition chemistry.[6]

A trigonal-prismatic coordination geometry, unprecedented for metal carbonyl derivatives, is adopted by **1** in the solid state (Figure 1).[7] The complex is monomeric with a methylene chloride of solvation present. No unusual intermolecular distances are observed. Pertinent intramolecular distances and angles are listed in Table I while least-squares planes of interest and associated dihedral angles are tabulated in Table II. Although no crystallographic symmetry is imposed on the complex, the observed structure conforms to virtual C_{2v} symmetry with the C_2 axis passing through the metal directly between the two carbonyl ligands.

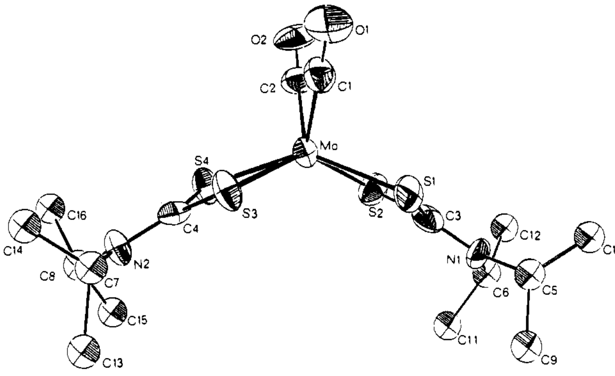

Figure 1. An ORTEP view of $Mo(CO)_2[S_2CN\text{-}i\text{-}Pr_2]_2$ showing the atomic labeling scheme.

Table I. Selected Bond Distances and Angles for $Mo(CO)_2[S_2CN\text{-}i\text{-}Pr_2]_2$

bond distances, Å		bond angles, deg	
Mo–C1	1.902 (8)	S1–Mo–S2	70.2 (1)
Mo–C2	1.919 (8)	S3–Mo–S4	70.6 (1)
Mo–S1	2.460 (2)	C1–Mo–C2	74.3 (3)
Mo–S2	2.456 (2)	S1–Mo–S3	98.7 (1)
Mo–S3	2.448 (2)	S2–Mo–S4	97.3 (1)
Mo–S4	2.451 (2)	S1–Mo–C1	85.7 (2)
C1–O1	1.180 (8)	S3–Mo–C1	84.3 (2)
C2–O2	1.175 (7)	S2–Mo–C2	83.7 (2)
N1–C3	1.329 (7)	S4–Mo–C2	83.9 (2)
N2–C4	1.309 (8)	Mo–C1–O1	177.4 (7)
		Mo–C2–O2	177.5 (6)

Table II. Dihedral Angles between Selected Least-Squares Planes

defining planes	dihedral angle, deg
MoS1S2:MoS3S4	135
MoS1S2:MoC1O1C2O2	113
MoS3S4:MoC1O1C2O2	112
MoC1O1C2O2:S1S2S3S4	91

Previous trigonal-prismatic monomers have been identified only for unusual complexes[8] involving severe ligand steric constraints[9] or tris(1,2-dithiolato)metal derivatives where interligand S···S interactions may play a unique role.[10] Note that the interligand S···S distances in **1** range from 3.68 to 4.66 Å and substantially exceed the sum of van der Waals radii (3.60 Å).[11] Indeed, the

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[1] (a) Green, M. L. H. "Organometallic Compounds"; Chapman and Hall: London, 1968; Vol. 2, pp 1–6. (b) Colton, R. *Coord. Chem. Rev.* **1971**, *6*, 269. (c) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

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[4] Suitable single crystals were obtained by slow recrystallization of **1** from a saturated methylene chloride solution. The dark blue-green solid exhibits two strong infrared absorptions attributable to cis-carbonyl ligands at 1934 and 1842 cm^{-1}. Note that a KBr pellet prepared under aerobic conditions was purple in color and displayed intense infrared absorptions at 2015, 1938, and 1900 cm^{-1} attributable to $Mo(CO)_3[S_2CN\text{-}i\text{-}Pr_2]_2$ and a very strong absorption at 968 cm^{-1} attributable to $Mo(O)[S_2CN\text{-}i\text{-}Pr_2]_2$.

[5] Colton, R.; Scollary, G. R. *Aust. J. Chem.* **1968**, *21*, 1427.

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[7] The crystal selected was monoclinic, space group $P2_1/n$, with unit-cell dimensions $a = 10.287$ (4), $b = 13.204$ (3), $c = 19.410$ (5) Å, $\beta = 101.99$ (6)°, and $Z = 4$. Of the 5013 reflections monitored, 2366 independent reflections with $I > 3\sigma(I)$ were used in the structure solution and refinement which converged to 0.048 and 0.049 for R and R_w, respectively. The final difference Fourier map was featureless with the largest residual electron density only 0.31 e/Å^3.

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