

Figure 2. Schematic view of the transition moments of the two bands in Δ^5 -cholestene: O-C, the direction of polarization of λ_1 (the shorter wavelength) band; O-A, the direction of polarization of λ_2 (the longer wavelength) band; O-B, the projection of the direction of polarization of the λ_2 band on the plane of the double bond; AOC, the angle between the transition moment of the λ_2 band and the double bond axis; BOC and AOB, the respective in-plane and out-of-plane deviations from the double bond axis of the transition moment of the λ_2 band.

These figures are based on the X-ray data for Δ^4 -3-keto steroids.^{9,10}

Calculations of the directions of the λ_1 and λ_2 transitions were performed geometrically using the values of angles these transitions make with the molecular axis (angles α , Table I), the previously mentioned X-ray data, and the assumption that these λ_2 and λ_1 transitions form similar angles with the double bond axis in both Δ^5 - and Δ^4 -cholestenes.

Since the α angles for λ_1 transitions in Δ^5 - and Δ^4 -cholestenes are 60 and 40°, respectively (Table I), it follows that the polarization of this transition is along the double bond axis. On the other hand, it is clear from the data of Table I that the λ_2 transition cannot be along the double bond axis.

Using similar geometrical consideration we have found that the λ_2 transition forms an angle of *ca.* 17° with the double bond axis, and an angle of 14° with the plane of the double bond; the projection of this transition on the double bond plane falls at an angle of 10° with the axis of the double bond (Figure 2).

The same directions for the transition moments were obtained also for Δ^4 - and Δ^5 -androstene derivatives which possess different orientations in the stretched films than those of the corresponding cholestenes (Table I).¹¹

Thus, we may conclude that olefins having symmetrically substituted double bonds show in the uv two bands of similar intensity, both of which are polarized along their double bond. In the unsymmetrically substituted olefins, however, only the shorter wavelength band, λ_1 , has in all cases a transition moment direction along the double bond, whereas in the longer wavelength band, λ_2 , the transition moment may deviate from this direction.

It is highly probable that the shorter wavelength band, λ_1 , is the conventional valence shell $\pi_z-\pi_z^*$ transition, whose polarization remains along the double bond and is not affected by unsymmetrical substitution.

However, the assignment of a transition to the λ_2 band is more problematic. We can rule out, for this band, the Rydberg type $\pi-3s$ ($\pi_z-\sigma^*$),^{2f} the valence shell $\sigma-\pi^*$,^{2g} or any other transition whose polarization should be perpendicular to the plane of the double bond.^{2g}

(9) H. Koyama, M. Shiro, T. Sato, Y. Tsukuda, H. Itazaki, and W. Nagata, *Chem. Commun.*, 812 (1967).

(10) No X-ray data are available for Δ^4 -cholestene itself.

(11) Since X-ray data are not available for other steroidal olefins, we have estimated polarization of some of them using Dreiding models. We have also found that in these compounds the λ_1 transitions are polarized along the double bond, but that the polarization of the λ_2 transition may assume other directions as well.

It was proposed by Clark⁶ that the higher wavelength band in a symmetrically substituted olefin, bicyclohexylidene, corresponds to a $\sigma-\sigma^*$ transition which is polarized along the double bond. Very recently Buenker, Peyerimhoff, and Hsu¹² suggested that a high intensity and low energy band in ethylene, which may be correlated with our λ_2 band, is due to the Rydberg type $\pi-3p_y$ transition ($\pi_z-\pi_y^*$) of 1B_g symmetry. This transition is formally allowed only in olefins twisted in the ground state and thus corresponds to a nonvertical transition in planar olefins. It may be expected that the unequal substitution of the double bond will have greater effect on the polarization of this Rydberg type band than on the valence type $\pi_z-\pi_z^*$ band.

(12) R. Y. Buenker, S. D. Peyerimhoff, and H. L. Hsu, *Chem. Phys. Lett.*, 11, 65 (1971).

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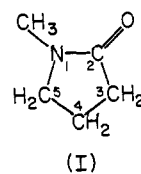
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Barrier to Internal Rotation of *N*-Methylpyrrolidone¹

Sir:

We wish to report the first known case of a methyl rotor attached to an intrinsically asymmetric framework with a nearly zero barrier to internal rotation.² The far-infrared spectrum of *N*-methylpyrrolidone (I) shows



a vast series of bands, at least one every wave number below 350 cm^{-1} . Such a large number of bands for a molecule of this size could only come from one of two possible kinds of motion, nearly free pseudorotation³ of the ring as a whole or nearly free internal rotation of the methyl group. However, the nitrogen-carbon amide bond is thought to be partially double bond in character and is expected to have a very high torsional force constant. This would rule out a free pseudorotation. Nearly free internal rotation is the only remaining possibility.

The spectrum of I in benzene shows intense peaks at about 175 and 310 cm^{-1} and a series of weaker bands extending down to the lower wavelength limit of our spectrometer. The 175- cm^{-1} band is assigned as ring bending (the out-of-plane motion of methylene group 4) and the 310- cm^{-1} band as the twisting motion of the ring (methylene group 3 moves above the plane while methylene group 5 moves below it and the amide group twists in the opposite sense). The solution

(1) Supported in part by the National Science Foundation.

(2) Methyl isocyanate with a barrier of 49 cal/mol [R. F. Curl, Jr., V. M. Rao, K. V. L. N. Sastry, and J. A. Hodgeson, *J. Chem. Phys.*, 39, 3335 (1963)] can be thought of as a slightly perturbed linear molecule; *m*-fluorotoluene with a barrier of about 47 cal/mol [H. O. Rudolph, and A. Trinkaus, *Z. Naturforsch.*, A, 23, 68 (1968)] as a perturbed toluene.

(3) J. A. Greenhouse and H. L. Strauss, *J. Chem. Phys.*, 50, 169 (1969).

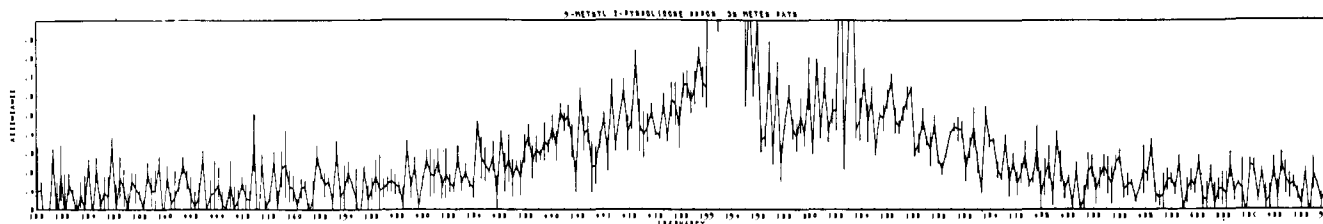


Figure 1. The infrared spectrum of *N*-methyl-2-pyrrolidone vapor from 100 to 200 cm^{-1} . The spectrum is of 39 m of gas at about 40°. The lines drawn on the spectrum are an indication of the noise level. The immense amount of structure seen in the spectrum is real.

spectrum also shows a complex series of bands with about a ten wave number spacing from 100 cm^{-1} to the lower limit of our spectrometer.

Under about 0.3- cm^{-1} resolution the spectrum of the gas phase splits into a vast series of lines. Part of this spectrum is shown in Figure 1. The number of bands and the spread of these bands over a few hundred wave number range in the gas-phase spectrum as well as the features of the liquid-phase spectrum can be explained by assigning the bands to transitions due to simultaneous changes of 0 or ± 1 in three quantum numbers: n_1 , the quantum number for the ring bending; n_2 , the quantum number for the ring twisting; and m , the quantum number for the internal rotation of the methyl group. The spectrum is made complex by the complex nature of the motion of each low-frequency mode and by the large interactions among them. The out-of-plane bending has been predicted to have a double minimum potential.⁴ The complexity of the spectrum makes a detailed assignment difficult, but it is the point of this note that the qualitative features of the spectrum cannot be explained without assuming a methyl rotation unhindered by a significant barrier. The spectrum we observe is qualitatively similar to the infrared spectra observed in molecules known to contain nearly free rotors.⁵ (Some difficulties in interpreting the details of the spectra of even the much simpler molecules such as CH_3NO_2 remain unresolved!⁵)

It is difficult to put a lower limit on the barrier to internal rotation but nitromethane with a barrier of 6 cal and methylboron difluoride with a barrier of 14 cal show similar series of bands and so we postulate a barrier of this order of magnitude. All known molecules with barriers of this magnitude have been molecules in which there can be no threefold term in the barrier to internal rotation because of the symmetry of the molecule. This is not the case for our molecule and reasonable guesses for the barrier for the $\text{C}^\alpha\text{-N}$ bond of a polypeptide, for example, are on the order of 1000 cal/mol.⁶ We cannot use the perturbation arguments of footnote 2 to explain the difference between our expectations and the observed result.

Instead we offer the following rationalization. Consider the methyl group rotated so that two of its hydrogens point at the two hydrogen atoms of methylene group 5. This would be expected to be a conformation of high energy, perhaps 1000 cal/mol above the minimum. However, in this configuration the remaining

hydrogen of the methyl group points at the carbonyl oxygen. If we postulate an attraction between the hydrogen and the oxygen atoms,⁷ we can explain the very low barrier as due to an "accidental" cancellation of the attractive and repulsive effects of the groups surrounding the methyl group.

Acknowledgment. It is a pleasure to acknowledge helpful conversations with Professors W. D. Gwinn, K. S. Pitzer, and A. Streitwieser, Jr.

(7) R. B. Davidson and L. C. Allen, *ibid.*, **54**, 2828 (1971), suggest such attraction in acetaldehyde.

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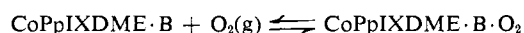
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A Pronounced Solvent Effect on the Reversible Oxygenation of a Cobalt(II) Porphyrin System

Sir:

Numerous reports of 1:1 reversible oxygen complexes of cobalt(II) have appeared in recent years.¹ Although all of these complexes bind oxygen at low temperatures, only coboglobin^{2,3} and a limited number of the cobalt Schiff-base complexes⁴⁻⁶ reversibly bind oxygen 1:1 at room temperature. Many of the non-protein cobalt complexes either lose oxygen or oxidize to a dimeric $\text{Co}^{\text{II}}\text{-O}_2\text{-Co}^{\text{III}}$ complex and/or other Co^{III} species. The ability of metal porphyrins to reversibly bind oxygen is of great biological significance since they are closely related to the oxygen carrying hemoproteins and coboglobin.

The reversible binding of oxygen to Co(II) porphyrins may be understood in terms of the equilibrium



$$K = [\text{CoPpIXDME}\cdot\text{B}\cdot\text{O}_2]/[\text{CoPpIXDME}\cdot\text{B}]p_{\text{O}_2}$$

where CoPpIXDME = cobalt(II) protoporphyrin IX dimethyl ester and B = base, e.g., pyridine, 1-methylimidazole ($\text{CH}_3\text{-Im}$), dimethylformamide (DMF), etc.⁷

(1) R. G. Wilkins, *Advan. Chem. Ser.*, **No. 100**, 111 (1971), and references cited therein.

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(6) J. Landels and G. A. Rodley, *Syn. Inorg. Metal. Org. Chem.*, **2**, 65 (1972).

(7) Although esr spectral evidence for six-coordinate Co(II) porphyrins at higher ligand concentrations at 77°K has been presented [F. A. Walker, *J. Amer. Chem. Soc.*, **92**, 4235 (1970)], esr data obtained

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