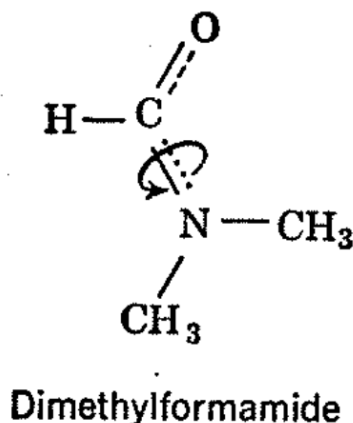


4.5: Rates of Rotation Around -CO-N- Bonds of Amides



Of extraordinary interest and importance is the use of NMR methods to determine rates of rotation around single bonds.⁴ The first observations of this kind were made with dimethylformamide. The spectrum of dimethylformamide at room temperature is shown in Fig. 4-7. At low fields, there is a one-proton resonance which arises from the aldehydelike hydrogen of the formyl group. The N-methyl proton resonances occur as two lines spaced about 10 cps apart at 40 Mc. The doublet methyl resonance might conceivably arise either from chemically different methyl groups or spin-spin coupling with the formyl proton. It will be noted from Fig. 4-7 that the formyl proton resonance is not split, so that the latter explanation is untenable. A chemical-shift difference has been established by the fact that at 30 Mc the two methyl peaks are only 7 cps apart. The knowledge that the separate methyl resonances arise from methyl groups in different chemical and magnetic environments forces the conclusion that there is restricted rotation around the -CO-N: bond of dimethylformamide. This is quite reasonable because resonance interaction between the carbonyl group and the unshared electron pair on nitrogen will tend to make all the atoms of the molecule lie in one plane, except for the protons on the methyl group. If the amide group is planar, one methyl group must be cis and the other trans to the carbonyl oxygen, and if rotation is slow about the -CO-N: bond, then the protons of each methyl will give a separate resonance line. On heating, the rate of rotation around the -CO-N: bond increases and finally the separate methyl resonances coalesce to a single line, as shown in Fig. 4-7. Considerable work has been done to determine the activation energy for rotation in dimethylformamide, and although the precision obtained by a given investigator is satisfactory, there are considerable discrepancies among the reported values.^{2,6} This may possibly be due to effects of impurities.

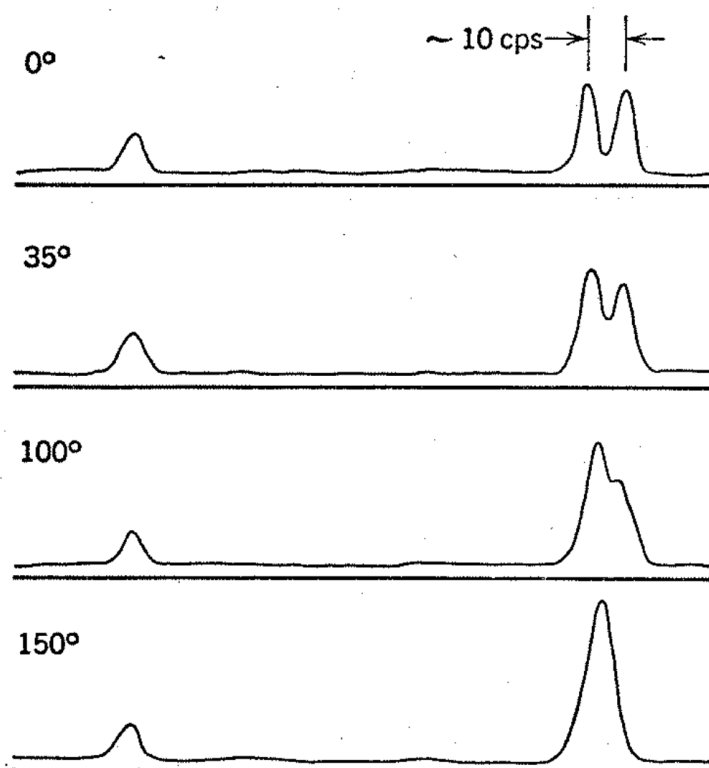
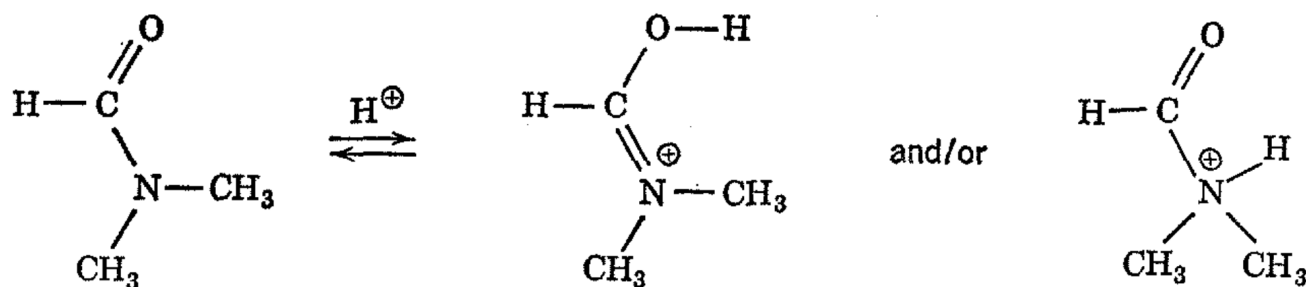


Fig. 4-7. Proton spectrum of dimethylformamide as a function of temperature at 40 Mc.

Phillips⁷ has made elegant use of the slowness of rotation around the -CO-N: bond of dimethylformamide to learn how the molecule accepts a proton in forming the conjugate acid. As shown in the following equation, the proton could add to either the oxygen or the nitrogen.



One could well argue that nitrogen is intrinsically more basic than oxygen, so that the nitrogen might be the favored position, even though addition of the proton to nitrogen would mean loss of resonance energy associated with the interaction of the nitrogen unshared electron pair with the carbonyl group. On the other hand, it could be argued that the amide oxygen would be more prone to accept a proton than usual for carbonyl oxygen because the resulting conjugate acid would be substantially stabilized by resonance involving the unshared electron pair on nitrogen.

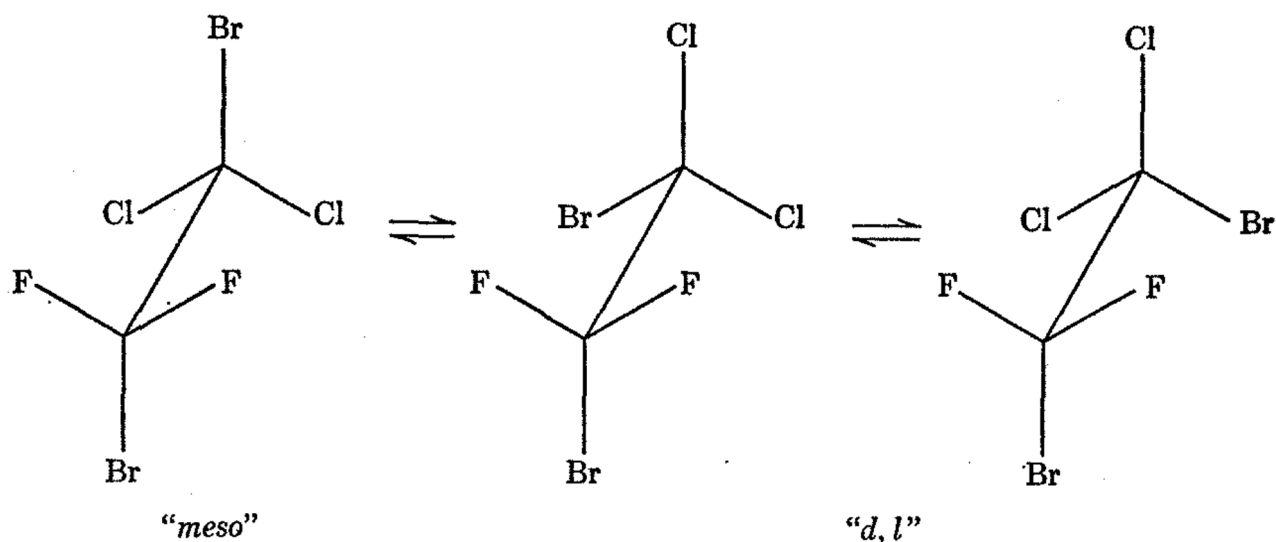


Fig. 4-8. Rotational conformations of 1,1-difluoro-1,2-dibromo-2,2-dichloroethane.

Phillips recognized that if the proton adds to nitrogen, this would destroy the double-bond character of the -CO-N: bond and reduce the barrier to rotation to the very low value expected for a C-N single bond. On the other hand, if the proton adds to oxygen, then the amount of double-bond character in the -CO-N: bond would be increased and rotation would be more difficult. Experimentally, it is observed that the rate of rotation around the single bond in dimethylformamide in strong acid solution is not increased compared with neutral solution, and therefore the added proton is preferentially attached to oxygen.

A number of interesting studies of restricted rotation in nitrites, N-nitrosamines, and oximes have been reviewed by Phillips.⁴

4 W. D. Phillips, Ann. N.Y. Acad. Sci., 70, 817 (1958).

5 W. D. Phillips, J. Chem. Phys., 23, 1363 (1955).

6 Research by J. N. Shoolery reported in Varian Associates Tech. Bull., 2, 7 (1957).

7 Private communication from W. D. Phillips. Similar studies have been made by G. Fraenkel and C. Niemann, Proc. Nat. Acad. Sci., 44, 688 (1958).

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