

130° and was identical with the 3-aminocoumarin obtained by the method of Linch.

Yield 80 per cent. of theory.

Other aldehydes are being investigated.

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¹ *Annal.*, 1904, **337**, 222-35; *C.A.*, 1905, **1**, 131.

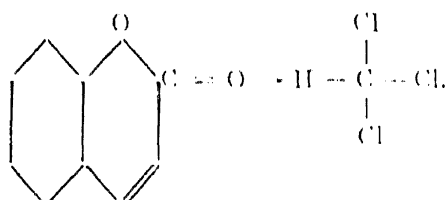
² Linch, *J.C.S.*, 1912, T., 1758.

³ Linch, *loc. cit.*

Molecular Complexes in Chloroform Solution

THAT polar solvents are capable of forming complexes with suitable solutes has been fairly well recognised and various methods have been used for detecting their formation.¹ Chloroform is said to undergo these combinations through a co-ordinate bond involving its H atom.²

It was recently shown by us³ that the Raman line for the C = O group of coumarin in chloroform solution undergoes a marked shift towards the exciting line as compared with a carbon tetrachloride solution which was taken as the standard. The phenomenon was explained as due to the formation of hydrogen bond as below:—



As a result of this complex formation, in which the oxygen atom of the C = O is the donor and the hydrogen of chloroform the acceptor, the C = O bond is diminished in strength and the frequency is reduced. In the course of the extension of this work a large number of carbonyl compounds have been studied in carbon-tetrachloride and chloroform solutions. In the case of saturated ketones, acids or esters no

difference between the two solvents was noticed. Obviously with these substances complex formation, if it took place at all, could not produce sufficient change to be exhibited in the Raman spectra. On the other hand, in unsaturated carbonyl compounds such as those given in the table below there was appreciable effect which could be noticed by a definite broadening of the line and a shift towards lower frequencies.

TABLE I

The C = O frequencies are given in $\Delta\bar{\nu}$

Substance	Pure state	Chloroform solutions	Carbon tetrachloride solutions
Benzylidene acetone	1668	1653	1670
Methyl cinnamate	1712	Diffuse mass towards shorter wave-lengths	1712
Ethyl cinnamate ..	1712	Do.	..
Phenyl cinnamate	1740	1722	1740
Coumarin ..	1708, 1731	1720	1742

Further work in regard to the detailed study of these is in progress. The close resemblance between coumarin and phenyl cinnamate in this respect is noteworthy and finds an easy explanation in the similarity of their structures.

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¹ Macleod, *Trans. Farad. Soc.*, 1934, **30**, 482; Macleod and Wilson, *ibid.*, 1935, **31**, 596; Glasstone, *ibid.*, 1936, **31**, 200; Bramley, *J.C.S.*, 1916, **109**, 11-14 and 343-519; Smith and Berkman, *Proc. Roy. Acad. Sci.*, Amsterdam, 1918, **401**, 21; Dolezalek, *Z. Physik. Chem.*, 1910, **71**, 191.

² Walter Gordy, *Nature*, 1938, **142**, 831.

³ Murli and Seshadri, *Proc. Ind. Acad. Sci.*, 1938, **8**, 519.