303. *Organic Fluorine Compounds. Part V.* Infrared Studies on Fluoropyruvic Acid and Related Compounds.*

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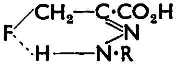
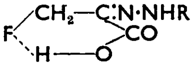
The infrared spectrum of fluoropyruvic acid and related compounds reveals that in the acid a hydrogen bond exists between the carbonyl and the carboxyl group, whilst in the corresponding 2 : 4-dinitrophenylhydrazones and semicarbazones hydrogen bonding can occur between the fluorine atom and either the carboxyl or the NH group.

The carbonyl absorption of pyruvic acid (capillary liquid layer) lies at 1723 cm.$^{-1}$.

In contradistinction to fluoropyruvic acid, its 2 : 4-dinitrophenylhydrazone and its semicarbazone show the infrared vibration of the C–F linkage, which usually [1] absorbs between 1010 and 1120 cm.$^{-1}$, at 991 and 978 cm.$^{-1}$, respectively. This observation (which has been mentioned briefly, but evidently not clearly enough,[2] by Mager and Blank [3]) invited a further study, especially in view of the unusual biological properties of the semicarbazone of fluoropyruvic acid.[4]

It appears reasonable to assume that the shift of the C–F band is due to hydrogen bonding which will tend to weaken the C–F linkage and, therefore, lower its characteristic frequency. The possibility of hydrogen bonding between a fluorine atom and a hydroxyl group has been suggested before.[5,6] In the present case, two types of hydrogen bonding are possible, involving the NH group or the carboxyl group, as indicated in (I) and (II), respectively.

(I) 

 (II)

[R = CO·NH$_2$ or C$_6$H$_3$(NO$_2$)$_2$]

respectively. In order to clarify this point, the infrared spectra of the 2 : 4-dinitrophenylhydrazone of methyl fluoropyruvate and of the *N*-methyl-2 : 4-dinitrophenylhydrazone of fluoropyruvic acid were measured. In the former, bands at 992 (medium) and 1052 cm.$^{-1}$ (strong) have been observed, probably corresponding to a hydrogen-bonded and to a " free " C–F linkage, respectively. The hydrogen bonding can only involve the NH of the phenylhydrazone grouping, but it appears that this bond is weak, perhaps because the *o*-nitro-group competes with the fluorine atom for the hydrogen bond. In the *N*-methyldinitrophenylhydrazone of fluoropyruvic acid, a single strong band at 973 cm.$^{-1}$ represents the hydrogen-bonded C–F frequency : in this case, only the carboxyl group [according to (II)] can supply the hydrogen. One can, therefore, conclude, that form (II) is more stable than (I), and that (I) only applies when no free carboxyl group is available.

The assignment of the frequency in the 973—992 cm.$^{-1}$ region to the stretching of the hydrogen-bonded C–F linkage is supported by the spectrum of pyruvic acid *N*-methyl-2 : 4-dinitrophenylhydrazone, which, like the dinitrophenylhydrazones of pyruvic acid and methyl pyruvate, shows no band in that region.

There remains one point to be discussed. Whilst in methyl fluoropyruvate the location of the C–F bond at 1046 cm.$^{-1}$ is normal (no hydrogen bonding possible), one would expect a shift of this peak in the case of fluoropyruvic acid. However, in this compound also the C–F bond has been found at 1035 cm.$^{-1}$ (Thomas [2] gives 1022 cm.$^{-1}$, but his measurements were carried out on a solution of the compound, whilst in the present investigation a solid capillary layer has been used). The absence of this shift is best ascribed to a structure in

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* Part IV, *J.*, 1955, 2190.

[1] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.
[2] Thomas, *Nature*, 1955, **175**, 424.
[3] Mager and Blank, *ibid.*, 1954, **173**, 126.
[4] Mager and Avi-Dor, unpublished results.
[5] Wulf, Liddel, and Hendricks, *J. Amer. Chem. Soc.*, 1936, **58**, 228.
[6] Park, Brown, and Lacher, *ibid.*, 1953, **75**, 4753.

which the carboxyl group is hydrogen-bonded to the ketonic carbonyl-oxygen either in the same or in a second molecule (formation of a dimer), thus leaving the C–F bond unaffected.

The difference in the hydrogen-bonded C–F frequency in the dinitrophenylhydrazones of fluoropyruvic acid (991 cm.$^{-1}$) on one hand, and in fluoropyruvic acid semicarbazone (978 cm.$^{-1}$) and *N*-methyldinitrophenylhydrazone (972 cm.$^{-1}$) on the other, is somewhat unexpected, but any attempt to explain this difference would be speculative.

The dinitrophenylhydrazones and *N*-methyldinitrophenylhydrazones described in this paper are well-defined crystalline substances. No *syn-anti*-isomerism of the type described recently by various authors [7] has been observed. It should be pointed out that the formation of hydrogen-bonded rings of type (I) presupposes that the substituents at the azomethine-nitrogen atom and the carboxyl (or ester) group are *trans* to each other.

In connection with these experiments, the carbonyl frequency of fluoropyruvic acid (solid capillary layer, obtained by cooling a thin molten layer of the acid) was measured as an intense, broad band centred at about 1723 cm.$^{-1}$. This value is considerably lower than that reported for pyruvic acid (1745 cm.$^{-1}$),[8] but lies rather in the region expected when one recalls that the interaction of the two carbonyl groups should increase only by very little the usual [9] frequency of 1715 cm.$^{-1}$. A further study of the spectrum of pyruvic acid (very thin liquid layer) showed the band to be at 1728 ± 4 cm.$^{-1}$, in agreement with the above figure for fluoropyruvic acid and the value (1726 cm.$^{-1}$) for 11 : 12-diketo-steroids.[10] The fluorine atom might have been expected to *raise* somewhat the carbonyl frequency, but it is perhaps difficult to predict accurately the effect of the interaction of the various polar linkages, especially if the molecule is dimeric (see above).

EXPERIMENTAL

Fluoropyruvic acid and its methyl ester were prepared according to Mager, Blank, and Bergmann.[11] The infrared spectrum of the ester was measured in CCl_4 solution (0·06 g. in 1 ml.; 0·1-mm. cell).

The 2 : 4-*dinitrophenylhydrazone* of the methyl ester was prepared by the standard procedure,[12] though the yield was low. It formed orange-yellow crystals and melted, after recrystallization from alcohol, at 245° (Found: C, 39·8; H, 3·0; N, 18·8. $C_{10}H_9O_6N_4F$ requires C, 40·0; H, 3·0; N, 18·7%). The infrared spectrum was measured in a paraffin oil mull; bands were observed at 992, 1052, 1077, and 1144 cm.$^{-1}$.

N-Methyl-2 : 4-dinitrophenylhydrazine was prepared according to Blanksma and Wackers,[13] from methylhydrazine [14] and chloro-2 : 4-dinitrobenzene. Recrystallized from ethyl alcohol, it melted at 141°.

Fluoropyruvic Acid N-*Methyl*-2 : 4-*dinitrophenylhydrazone*.—To a solution of the hydrazine derivative (1 g.) in 95% ethanol (50 ml.), a solution of fluoropyruvic acid (0·5 g.) in ethanol (10 ml.) and 2 drops of concentrated sulphuric acid were added. The mixture was refluxed for 10 min. and evaporated *in vacuo* until an oil separated. This was triturated with, and recrystallized from ethyl acetate; it formed yellow crystals, m. p. 158—159° (Found: C, 40·7; H, 3·2. $C_{10}H_9O_6N_4F$ requires C, 40·0; H, 3·0%). The ultraviolet spectrum showed a broad maximum at 380 mμ (log ε 3·74) (in EtOH). The infrared spectrum was measured on a mull in paraffin oil. The following bands were observed in the 900—1220 cm.$^{-1}$ region (the relative absorbances are given in parentheses): 909 (0·37), 973 (0·65), 1062 (0·43), 1112 (0·53), 1146 (0·50), 1175 (0·55).

Pyruvic Acid N-*Methyl*-2 : 4-*dinitrophenylhydrazone*.—The above method was applied to pyruvic acid. The *product* separated from butanol as yellow crystals, m. p. 164° (decomp.) (Found: C, 42·5; H, 3·6; N, 20·4. $C_{10}H_{10}O_6N_4$ requires C, 42·6; H, 3·6; N, 20·0%). Ultraviolet

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[7] Stewart, *Biochem. J.*, 1953, **55**, 26; Isherwood and Cruickshank, *Nature*, 1954, **173**, 121; Ramirez and Kirby, *J. Amer. Chem. Soc.*, 1954, **76**, 1037; van Duin, *Rec. Trav. chim.*, 1954, **73**, 78; Denny and Reid, *Chem. and Ind.*, 1954, 755; Khromov-Borisov, *Chem. Abstr.*, 1955, **49**, 8257.

[8] Randall, Fowler, Fuson, and Dangl, "Infrared Determination of Organic Structures," van Nostrand, New York, 1949, p. 104.

[9] Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1954, p. 122.

[10] Jones, Humphries, and Dobriner, *J. Amer. Chem. Soc.*, 1949, **71**, 241.

[11] Mager, Blank, and Bergmann, *J.*, 1955, 2190.

[12] Shriner and Fuson, "Identification of Organic Compounds," 3rd edn., Wiley, New York, 1948, p. 131.

[13] Blanksma and Wackers, *Rec. Trav. chim.*, 1936, **55**, 655.

[14] *Org. Synth.*, Coll. Vol. II, p. 395.

spectrum: $\lambda_{max.}$ 383 mμ (log ε 4·46) (in EtOH). Infrared spectrum, measured as in the preceding case: 919 (0·55), 941 (0·37), 1005 (0·72), 1038 (0·50; shoulder), 1061 (0·80), 1100 (0·55), 1141 (0·82), 1203 (0·98).

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