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MAGNETIC NON-EQUIVALENCE IN THE METHYLENE GROUP OF AN ETHYL ESTER

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At room temperature in deuterochloroform solution, ethyl 2-(2,4-dinitrophenyl) acetoacetate exists in the enol form, as shown* by a one proton singlet at 13.18 δ in the proton magnetic resonance (p.m.r.) spectrum (1), and the absence of any strong ν C=O band above 1700 cm^{-1} in the infra-red. The methylene protons show magnetic non-equivalence (MNE), and the ethyl ester group comprises an ABX_3 p.m.r. spectrum. This was confirmed by double resonance experiments (Fig. 1). Spin-decoupling proved that the multiplet centred about 4.14 δ, and assigned to the methylene protons, is coupled to the three proton triplet at 1.14 δ. Spin tickling experiments (3) showed that J_{AX} ($=J_{BX}$) is of opposite sign to J_{AB}, consistent with J_{AB} being a geminal and J_{AX} a vicinal coupling constant. This information and the parameters deduced for the ethyl grouping of the enolic form by spectral analysis (4), are given in Table 1.

If the compound were in the keto form, MNE might have been anticipated (5), although it has not yet been observed in the keto form of an ethyl acetoacetate. Inspection of Dreiding molecular models showed that the observed MNE can readily be explained (cf 6) if the enolic

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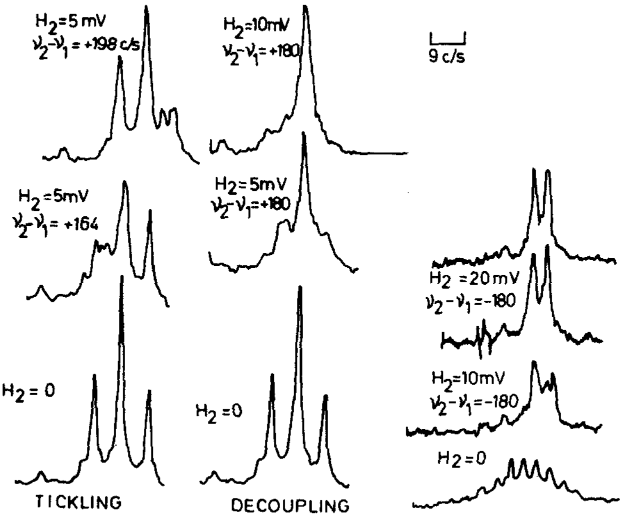
* All chemical shifts (δ) are in p.p.m. downfield from internal tetramethylsilane.

g. 1 FIELD SWEEP DOUBLE RESONANCE



Irradiating the 4·14δ multiplet and observing the 1·14δ triplet

Irradiating the 1·14δ triplet and observing the multiplet

TABLE 1

The p.m.r. Parameters of the ABX_3 Ethyl Group of Ethyl 2-(2,4-dinitrophenyl) acetoacetate at 33.4°C

Solvent	δX	δA (ppm)	δB	J_{AX} (c/sec)	J_{AB}
Deuterochloroform	1.14	4.06	4.22	± 7.26	∓ 10.80
Acetone	1.10	4.08	4.23	± 7.10	∓ 10.91
Acetonitrile	1.10	4.05	4.19	± 7.10	∓ 11.02

hydroxyl group is intramolecularly hydrogen-bonded either to the ester carbonyl (2) with twisting of the aromatic ring out of the plane of the chelate ring, or to the <u>ortho</u>- nitro- group. Since the two "nitro" infra-red vibrations at 1530 and 1350 cm^{-1} (in nujol mull) are "normal", the latter possibility is the less likely. However, in either case, MNE would not be expected in ethyl 2-(2,4,6-trinitrophenyl) acetoacetate. This compound was prepared and the methylene protons do not show MNE. A comparable observation has been made in the N,N-disubstituted acetamide series (7). Other related β-keto esters show no such MNE: ethyl 2-methylacetoacetate (8), ethyl 2-methylbenzoylacetate, ethyl 2-acetoxybenzoylacetate and ethyl 2-phenylacetoacetate. The last compound is an approximately 1:1 mixture of the enol and keto forms, neither showing MNE.

In acetone and acetonitrile, the p.m.r. spectrum of ethyl 2-(2,4-dinitrophenyl) acetoacetate indicated significant proportions of another form, showing no MNE. This was probably the intermolecularly hydrogen-bonded enolic form, since in deuteroacetone and deuteropyridine over the range -60° to +100°C, as the temperature is raised, the enol proton resonance broadens. This is presumably because the exchange between the intra- and inter-molecularly bonded forms becomes significant. At the same time, the MNE disappears.

EXPERIMENTAL

Proton magnetic resonance spectra were obtained at 60.004 Mc/sec and 33.4°C with a Perkin Elmer R-10, at other temperatures with a Varian Associate A-60 spectrometer. The J values recorded below are the measured splittings. The infra-red spectra were obtained in chloroform solution using a Perkin Elmer 337 spectrometer.

<u>Ethyl 2-(2,4-dinitrophenyl) acetoacetate</u> (9) Ethyl acetoacetate (130 g) was added dropwise to a stirred mixture of anhydrous ether (900 cc) and

sodium wire (23 g) during 45 min. After two hours, 2,4-dinitrochlorobenzene (80 g) in anhydrous ether (500 cc) was added dropwise, the mixture heated with stirring on a water bath for 5 hours, and then left overnight. Absolute ethanol (100 cc) was added with stirring and the solution then washed successively with water (3 x 1.1), 2% sodium hydroxide solution (4 x 500 cc) and water. The combined alkaline washings were acidified with nitric acid, and the precipitate was recrystallised from aqueous ethanol to give the ester, mp. 93-94° as bright yellow plates. (Found: C, 48.3; H, 4.2; N, 9.9. Calc. for $C_{12}H_{12}N_2O_7$: C, 48.6, H, 4.1; N, 9.5%). The proton magnetic resonance spectrum in deuterochloroform consisted of a singlet at 13.18 δ (1 proton); a doublet at 8.86 δ (J = 2.3 c/sec, 1 proton); a pair of doublets at 8.48 δ (J = 2.3, 8.5 c/sec, 1 proton); doublet at 7.58 δ (J = 8.5 c/sec, 1 proton); a multiplet at 4.14 δ (2 protons); a singlet a 1.94 δ (3 protons); and a triplet at 1.14 δ (J = 7.2 c/sec, 3 protons). The infra-red spectrum showed strong bands at 1660, 1610 and 1545 cm^{-1} with a weak band at 1735 cm^{-1}.

Ethyl 2-(2,4,6-trinitrophenyl) acetoacetate (10) This was obtained as a yellow crystalline compound, mp. 95-98°C. The proton magnetic resonance spectrum in deuterochloroform consisted of: a singlet at 12.98 δ (1 proton); a singlet at 8.84 δ (2 protons); a quartet at 4.12 δ (J = 7.2 c/sec, 2 protons); a singlet at 1.80 δ (3 protons); and a triplet at 1.13 δ (J = 7.2 c/sec, 3 protons). The infra-red spectrum showed strong bands at 1665, 1620 and 1550 cm^{-1}.

Ethyl 2-benzoyl propionate (11) This was obtained as a pale yellow liquid b.p. 158-62°/20 mm. The proton magnetic resonance spectrum in carbon tetrachloride consisted of: a complex (5 protons) centred at 8.0 δ and 7.5 δ; a quartet (J = 7.3 c/sec, 1 proton) at 4.33 δ; a quartet (J = 7.3 c/sec, 2 protons) at 4.03 δ; a doublet (J = 7.3 c/sec, 3 protons) at 1.40 δ; and a triplet (J = 7.3 c/sec, 3 protons) at 1.09 δ.

Ethyl 2-acetoxybenzoylacetate (12) This was obtained as a light yellow oil b.p. 120-125°/2 mm, and then purified by thin layer chromatography to acolourless oil. The proton spectrum in carbon tetrachloride consisted of: a complex (5 protons) at 8.0 and 7.6 δ; a singlet (1 proton) at 6.18 δ; a quartet (J = 7.4 c/sec, 2 protons) at 4.23 δ; a singlet (3 protons) at 2.18 δ; and a triplet (J = 7.4 c/sec, 3 protons) at 1.24 δ.

Ethyl 2-phenylacetoacetate (13) Obtained as a liquid b.p. 100-102°/1.5 mm. The proton spectrum in carbon tetrachloride consisted of: a complex (10 protons) at 7.2 δ; two quartets (J = 7.4 c/sec, each 2 protons) at 4.11 and 4.09 δ; two triplets (J = 7.4 c/sec, each 3 protons) at 1.18 and 1.08 δ; two singlets (each 3 protons) at 2.03 and 1.77 δ; a singlet (1 proton) at 4.60 δ; and a singlet (1 proton) at 13.05 δ.

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