COMMUNICATIONS

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Chirality in α- Dinitrophenyl -β- Keto Esters

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ABSTRACT

The complex methylene pmr spectra of some α- dinitrophenyl–β– keto esters is explained in terms of chirality of the molecules due to hindered rotation about aromatic carbon-aliphatic carbon bond. pmr and cmr data is reported in order to prove the conclusions.

INTRODUCTION

The NMR spectra of compounds which contain the groups $-CH_2 X-$ or $-C(CH_3)_2 X$ have been investigated by numerous authors and an excellent review of the subject has been given by Raban and Mislow[1]. Molecules which are chiral but not asymmetric may contain diastereotopic groupings. Nuclei which are diastereotopic must have different chemical shifts in either chiral or chiral solvents. Such nuclei are said to be anisochronous such as diethyl sulfite[2], cyclocarbinyl ethyl ether[3] offer striking examples of magnetic nonequivalance of methylene hydrogens in compounds of the type $R\text{-}CH_2 -O\text{-}CR_1 R_2 R_3$. Thus the pmr spectra of such methylene protons are often typical of AB rather then A_2 systems.[1]

In our studies, the investigation of enolisation of α-dinitrophenyl-β-keto esters by pmr we observed that the some of enolic form of said molecules exhibit complex methylene spectra and that was explained in terms of chirality due to the hindered rotation about aromatic carbon-enolic carbon bond.

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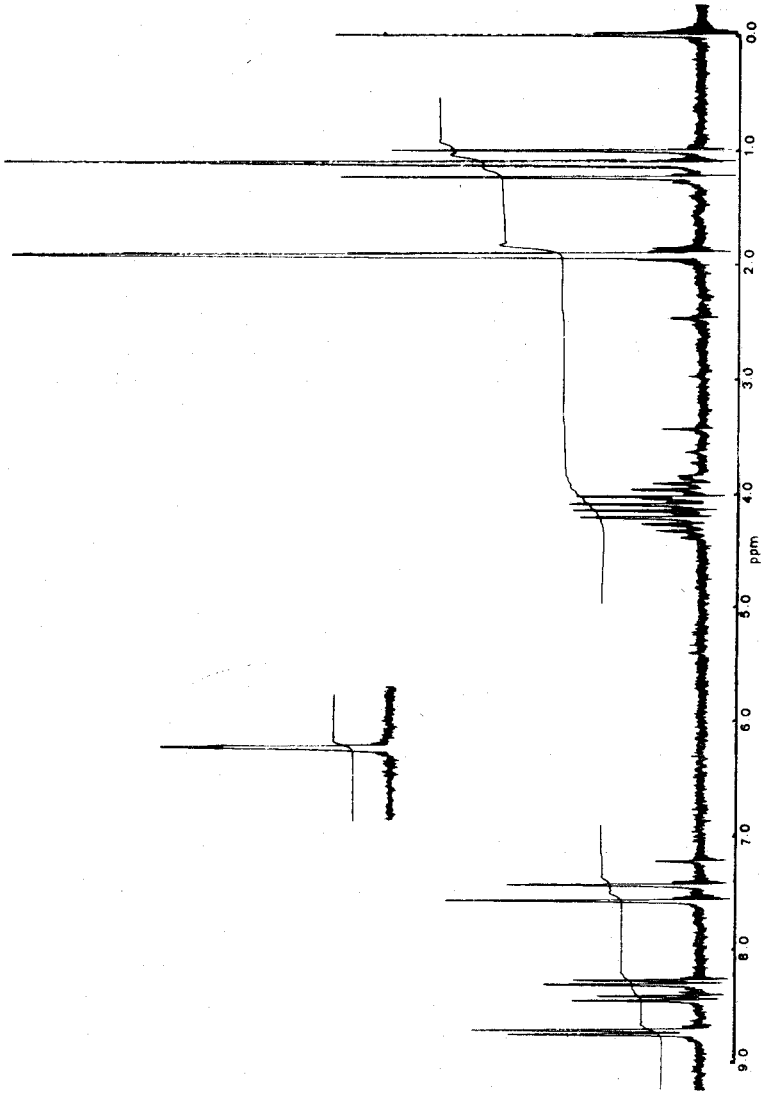
Figure-I. 60 MHz pmr spectra of α-2, 4-dinitrophenyl ethylacetoacetate in CDCl$_3$ (5 % Wt/vol) 40°C Ofset 360 Hz.
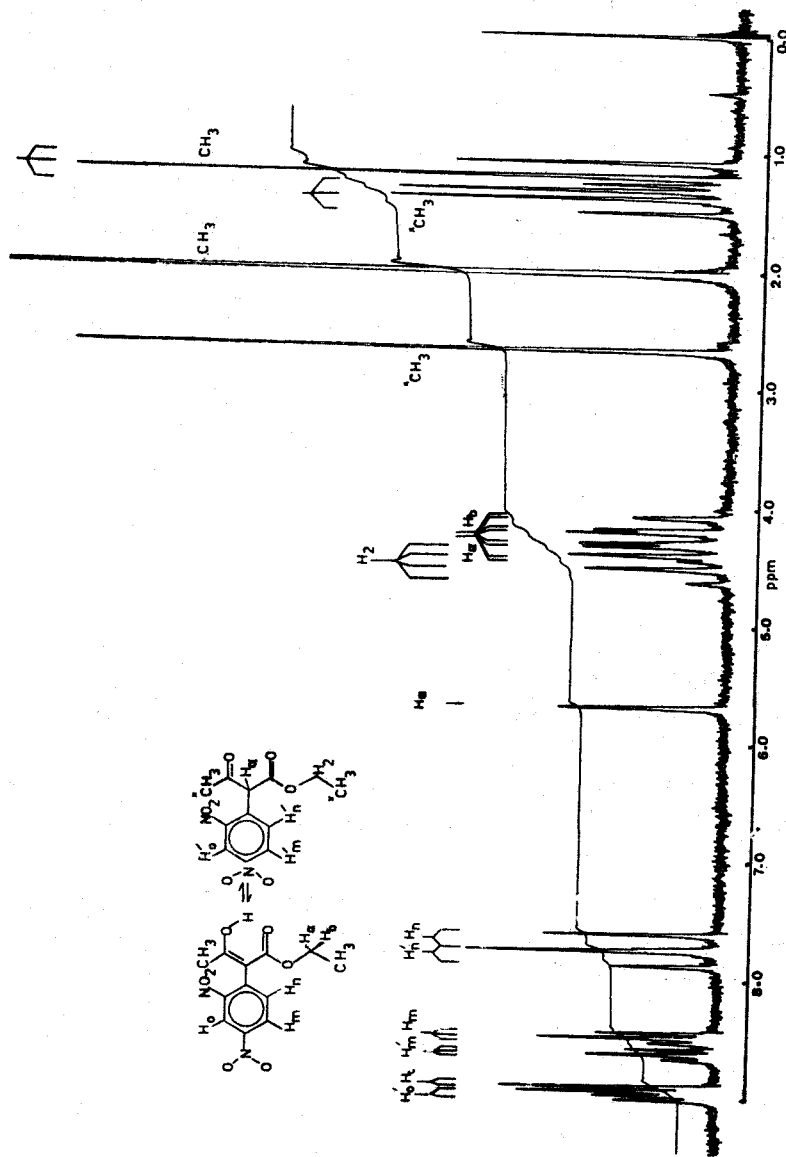
Figure-II. 60 MHz pmr spectra of α–2, 4–dinitrophenyl ethylacetoacetate in CF$_3$ COOH (5 % Wt/vol) at 40°C.

RESULTS AND DISCUSSIONS

Regarding both cmr and pmr spectra it seems strongly jus-
tified that α–dinitropbenyl–β–keto esters are at least 90 % enolic[6]
(Figure–1). However in strongly acidic solvents keto content of
such molecules increase up to 40 % (Figure–II).

It is now also proved that enol from of α– 2, 4-dinitropbenyl-
β–keto esters exhibit bipbenyl-like-isomerism[5] due to the chelation
of β–keto esters obviously behave as a plane which would be pre-
vented to rotate about aromatic carbon-enolic carbon bond.
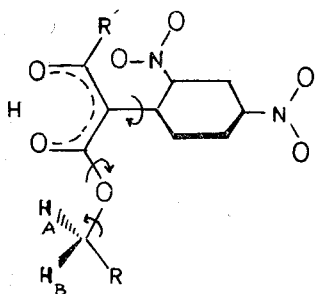
COMPND.	R	R^x
I	CH$_3$	CH$_3$
II	CH$_3$	C$_6$H$_4$NO$_2$

Chirality of the molecule arises from the chelate ring of the
β– keto esters becouse of the observation that in the presence of
piperidin the complex ABC$_3$ spectra of compound-I simplified to
A$_2$B$_3$ spectra due to intra moleculer proton transfer which de-
rease the stability of chelate ring resulting the rotation about
the Cα – COOR bond.

Hence, two rings in compound-I and II could not be coplanar
due to impingment of the o-nitro group of phenyl ring as well as
1, 3-substituents of chelate ring.
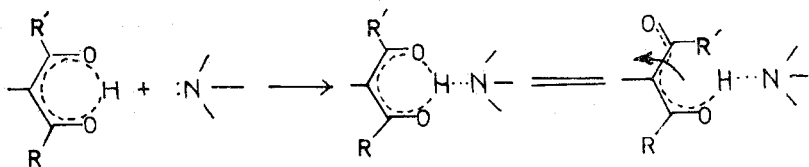
An O-substituent of one ring thus is located above the plane of the second ring, and if the second ring holds two different o-groups or 1, 3-substituents the substituents on the first ring is in an asymmetric environment. If that substituents contains methylene group its two protons thus become diastereotopic. Therefore methylene protons on ethoxy groups of α– 2, 4-dinitrophenyl-β-keto ethyl esters are diastereotopic and hence anisocronous. In such a case ABC_3 (or ABX_3) spin systems are expected and observed. Diastereotopic methylene protons resides in different environment even though the substituent rotates about chelate ring-substituent bond. The conformers of the ethoxy group about that bond (e.g., Ia-d Fig. III) will not necessarily be equally populated and the environments of the two protons are different in each conformer.
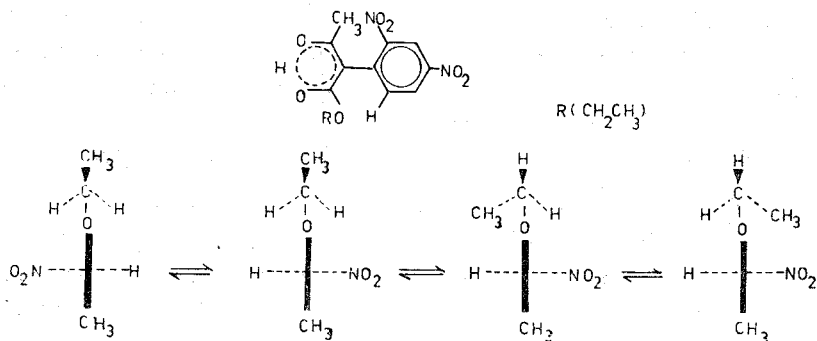

Figure – III. Conformers of chiral α– dinitrophenyl-β– keto esters

This could be seen from the pmr spectra of α– 2, 4-dinitrophenyl acetoacetate (compound-I) in wich the pmr spectra of such methylene protons typical AB rather than A_2 systems and complex spectra characteristic of AB part of ABC_3 spectra. The chemical shift between the two anisochronous protons $\Delta\delta_{AB}$ varies from 2 Hz to 11 Hz depending on the solvent and the structure of compound at 60 MHz with methyl-methylene coupling constants ca. 7, 0 Hz (Table-II).

After series of iterative calculations it was also demonstrated that methylene spectrum of compound-I could be fitted to with in experimental eror although there is a lower limit to $\Delta\delta_{AB}$ below which instrument resolution do not permit us. Therefore it was

Table – I. Chemical Shifts and Coupling Constants of Ethoxyl Protons of chrial α– dinit-rophenyl – β– keto esters, Compound-I and II in $CDCl_3$, 40°C, Values Hz down field from intermal TMS at 60 MHz.

Compound	R	R'	δH_A	δH_B	$\triangle \delta H_{AB}$	J_{AB}	δ_C
I	CH_3	CH_3	246.2	255.6	9.4	10.5	70
II	$NO_2 C_6 H_4$	CH_3	250.0	261.0	11.0	10.0	72

estimated ca. 2 Hz was the minimum value for the separations in theoretically calculated spectra (Figure-IV). Signs of coupling constants are, of course, assigned by analogy[8] (Figure-IV).

The origin of this magnetic nonequivalance has been subject of several investigations and two distinct chemical shift effects have been reported[1,2] a). An intrinsic assymetry effect ...... independent of rotamer populations b). Shift differences coused by dissimilar populations of various conformations or rotamers. It is still in question whether the former or the latter is alone responsible for magnetic nonequivalance. However, in our case effect of hindered rotations in the molecule is quite apparent.

Therefore we also examined pmr spectra of the similar compounds. The simple A_2B_3 methylene spectra of α– 2, 6-dinitrophenyl-β-keto esters (compound – III, IV) strongly proves that anisochronous behavior of methylene protons determined by the dissimilar o-substituents just as in biphenyl isomerism, similarly, 3– (2, 4-dinitrophenyl)-2, 4-pentandion (V) and α– 2, 4-dinitrophenylethylcyanoacetate (VI) give simple A_2B_3 spectra of ethyl group although the fact that the molecule is asymmetrical and likely to be the racemic mixture. It is also interesting to note that α– (2, 4-dinitrophenyl)-t-butyl acetoacetate (VII) gives a line from t-butyl group-due to the enantiotopic methyl groups-indicating that contribution of rotamers about the oxygen-carbon bond is quite significant on magnetic nonequivalance (Table-II), (Figure-III) which is although not affected from the rotations about oxygen-carbonyl bond that seems also restricted.

The most important factor for the magnitudes of the shift differences anisotropy associated with phenyl ring, nitro groups as well as ansaturated chelate ring. The ^{13}C magnetic resonance spectra of compound-I and II was also examined (Table-III).
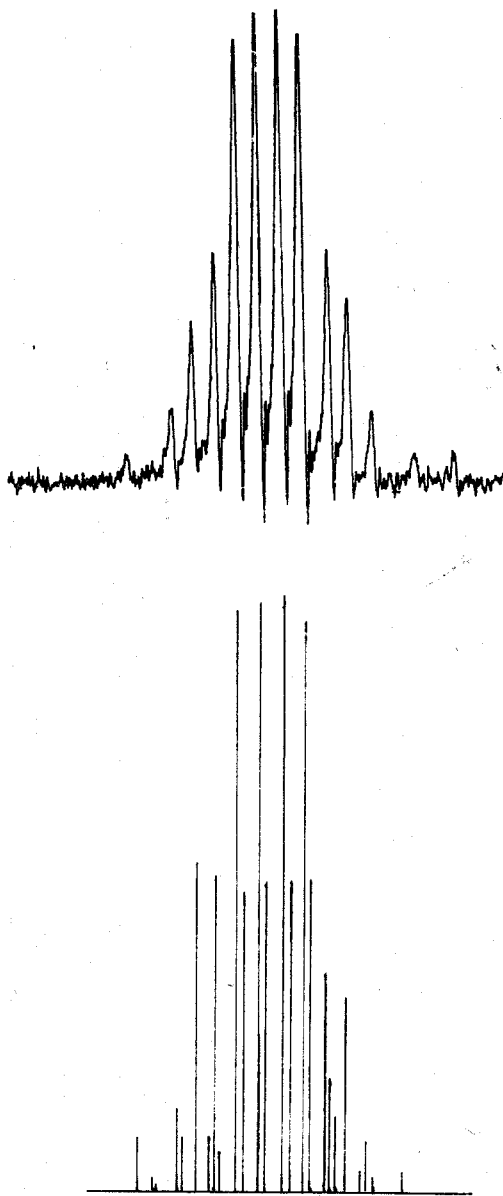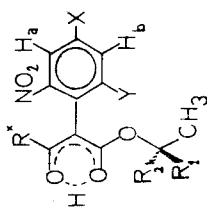
Figure-IV. Observed and calculated pmr spectra of 10 %/wt/vol solution of α– 2, 4–dinitrophenyl ethyl acetoacetate in CDCl₃ at 60 MHz TMS as an internal referance taken taken as zero.
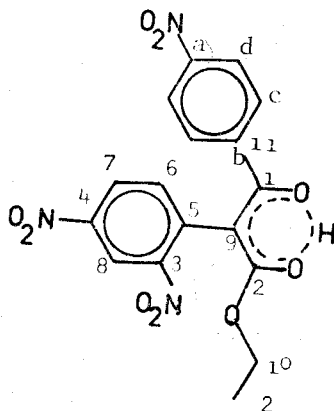
Table–II, pmr data of some α– dinitrophenyl-β-keto esters in CDCl₃ at 40°C. (II)

Y (No₂, H)
Rx (H, CH₃, C₆H₅)
R₁ (CH₃, H)
R₁ (CH₃, H)
X (No₂, H)

Compounds	δR₁	δR₂	δCH₃	δRx	δHb	δHa	δX	δY	δOH
(III) α– 2, 6-dinitrophenyl ethyl acetoacetate	250	250	67	107	482	482	458	—	777
(IV) α– 2, 6-dinitrophenyl ethyl benzoylacetate	253	253	71	428	468	468	452	—	798
(V) 3– (2, 4-dinitrophenyl) – 2, 4-pentandion	—	—	—	110	508	524	—	460	980
(VI) α– 2, 4-dinitrophenylethylcyanoacetate	256	256	76	—	518	534	—	484	334(x)
(VI) α– 2, 4-dinitrophenyl butylacetoacetate	83	83	83	117	504	523	—	452	809

(II) Chemical shift values are in Hz, aromatic protons given were calculated according to the first order approach for ABX pattern, and denoted by the delta scale, low fields shifts are shown as positive values relative to TMS as internal referance. Concentration of substance taken 2 % – 5 % in volume.

(X) Chemical shift value of methine proton.

PMR spectra were run on a VARIAN Associate Model A-60A spectrometer operating a frequency of 60 MHz.

Table – III. ^{13}C chemical shifts and relative intensities of compound-I and compound-II expressed in ppm from TMS intermal referance(x)

No^{13}C	Compound-I		Compound-II	
No^{13}C	δ^{13}C	Int.	δ^{13}C	Int.
1	174.2	56	169.8	30
2	169.9	54	169.4	40
3	150.0	16	149.6	6
4	148.0	20	146.9	12
a	–	–	148.7	14
5	136.5	33	139.4	38
b	–	–	135.8	107+
c	–	–	129.0	203
6	135.6	171	135.8	107+
7	126.8	179	126.7	81
d	–	–	123.0	154
8	120.0	171	120.0	75
9	99.8	59	102.0	17
10	61.4	180	62.5	103
11*	20.0	152	–	–
12	13.6	205	13.6	100

(x) Spectra were run on a VARIAN model XL–100 spectrometer operating in FT mode 25, 18 MHz.

(b) Aromatic carbon adjacent to carbonyl carbon in componnh

(+) Total relative intensity of Carbon-b and Carbon-6 since the signals are superimposed

(*) Carbon of methyl group in Compound-I

There is no signal separation at aliphatic range of the specrum although the fact that shift differences between conforemers are large and ^{13}C chemical shifts are extremely sensitive to contitutional environment[1].

ACKNOWLEDGEMENT

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ÖZET

α– dinitrofenil – β– keto esterlerin metilen grubunun karmaşık pmr spektrumunun kaynağı tartışılmış ve alifatik-aromatik karbon atomları arasındaki bağın etrafındaki dönmenin yapısal engellemeler nedeni ile sınırlandığı ve "bifenil" izomerlerine benzer "chiral" bir yapı oluşturduğu bu nedenle metilen protonlarının "diasterotopik" olarak davrandıkları anlaşılmıştır. Ayrıca bazı moleküllerde teorik yaklaşımlar ile pmr sabitleri bulunmuş denel sonuçlar ile karşılaştırılmışlardır.

Prix de l'abonnement annuel