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Abstract:

NMR spectra of the meso and d,l isomers of methyl-2,4-pentanedicarboxylate and of isotactic, heterotactic, and syndiotactic methyl-2,4,6-heptanetricarboxylate have been measured and analyzed. From the values of vicinal coupling constants the energy differences between various conformational structures of these isomers were estimated. The limitations of the procedure are discussed.

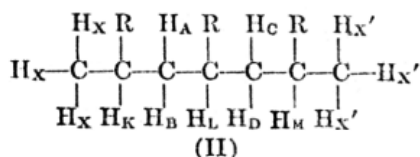
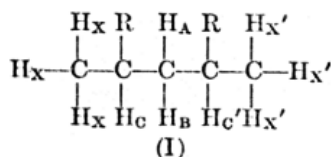
Molecular Structure and NMR Spectra of Stereoregular Poly(methyl Acrylate) Models.

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Synopsis

NMR spectra of the meso and *d,l* isomers of methyl-2,4-pentanedicarboxylate and of isotactic, heterotactic, and syndiotactic methyl-2,4,6-heptanetricarboxylate have been measured and analyzed. From the values of vicinal coupling constants the energy differences between various conformational structures of these isomers were estimated. The limitations of the procedure are discussed.

As part of a systematic study of conformational structures of vinyl polymer model compounds¹⁻³ the NMR spectra of the two-unit and three-unit models of poly(methyl acrylate) (PMA), namely the *d,l*- and meso isomers of methyl-2,4-pentanedicarboxylate (MPDC), and of syndiotactic, isotactic, and heterotactic isomers of methyl-2,4,6-heptanetricarboxylate (MHTC), were measured and analyzed. The preparation and purity of the samples used has been described elsewhere.^{4,5} The NMR spectra of these compounds were measured in CCl₄ and *o*-dichlorobenzene solution in a broad temperature range at 60 Mc. on a INM-3-60 spectrometer. In order to simplify analysis, some of the room-temperature spectra were re-measured at 100 Mc. on a Varian HA-100 instrument. Representative spectra are shown in Figures 1 to 5. The determination of conformational structure was based mainly on an analysis of the methylene proton band.



The proton spin system of meso-MPDC (I) involves one relatively strong geminal coupling with $J_{AB}/\delta_{AB} = 0.18$ (at 100 Mc.) and an even stronger

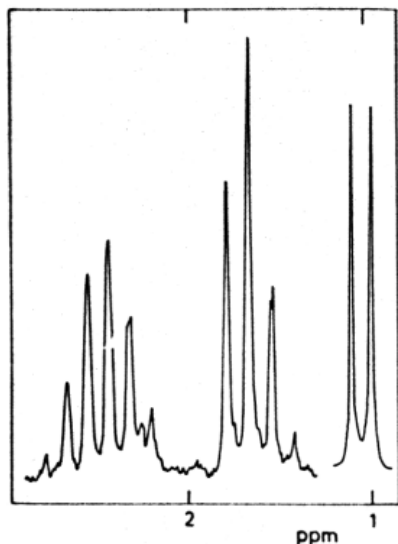


Fig. 1. NMR spectrum, 60 Mc., of the *d,l*-MPDC in *o*-dichlorobenzene solution at 20°C.

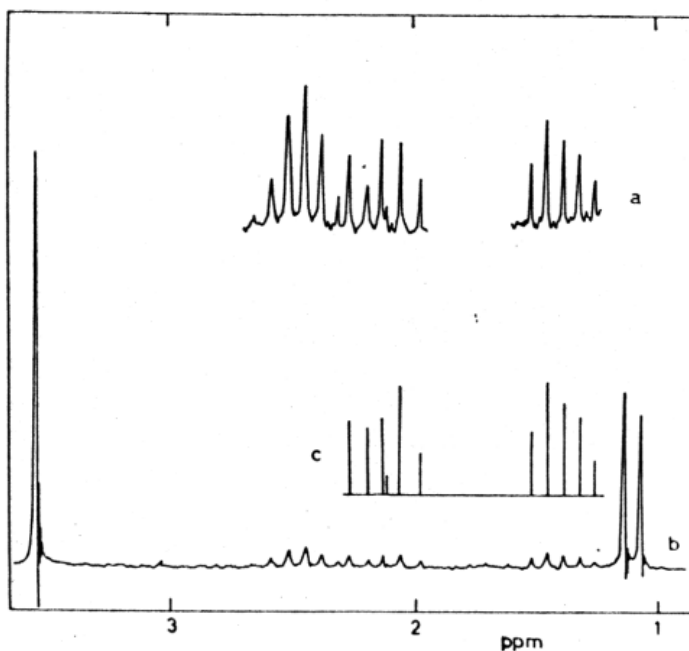


Fig. 2. NMR spectrum, 100 Mc., of *meso*-MPDC in *o*-dichlorobenzene solution at 26°C.: (a), (b) observed; (c) calculated.

vicinal coupling with $J_{BC}/\delta_{BC} = 0.21$ in addition to two weaker ones, $J_{AC}/\delta_{AC} = 0.07$ and $J_{CX}/\delta_{CX} = 0.05$. In its analysis the complete ten-spin system has therefore to be considered. However, the analysis of this system may be simplified by an extension of the effective-frequency method of Pople and Schaefer,⁶ owing to the weakness of the CX interaction and to the equality of the three J_{CX} coupling constants. The methylene proton band of (I) can be analyzed as a superposition of sixteen ABCD four-spin

systems by using for ν_C and ν_D the $\nu_C(x)$ and $\nu_C(x')$ effective frequencies corresponding to the 4×4 possible $F_z(X)$ and $F_z(X')$ states of the methyl protons. The 16 components of each band corresponding to one four-spin transition remain unresolved in the experimental spectrum and merely

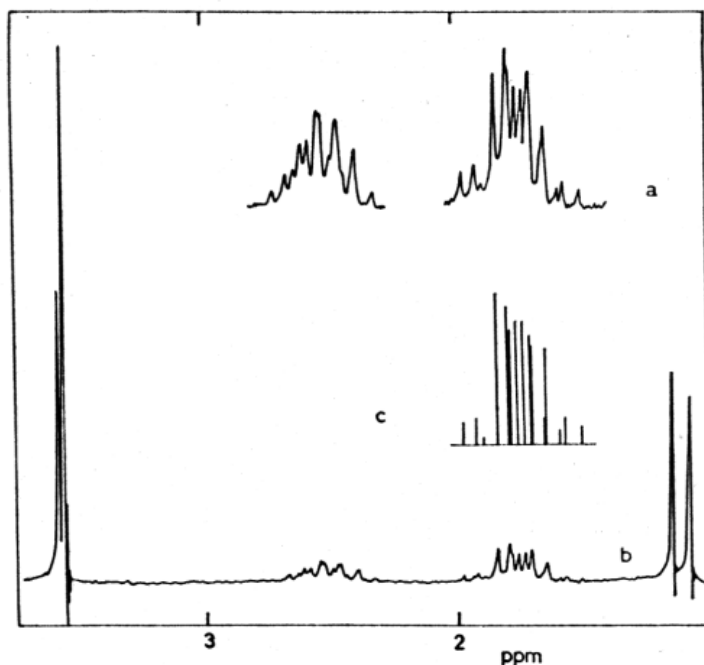


Fig. 3. NMR spectrum, 100 Mc. of syndio-MHTC in *o*-dichlorobenzene solution at 26°C.: (a), (b) observed; (c) calculated.

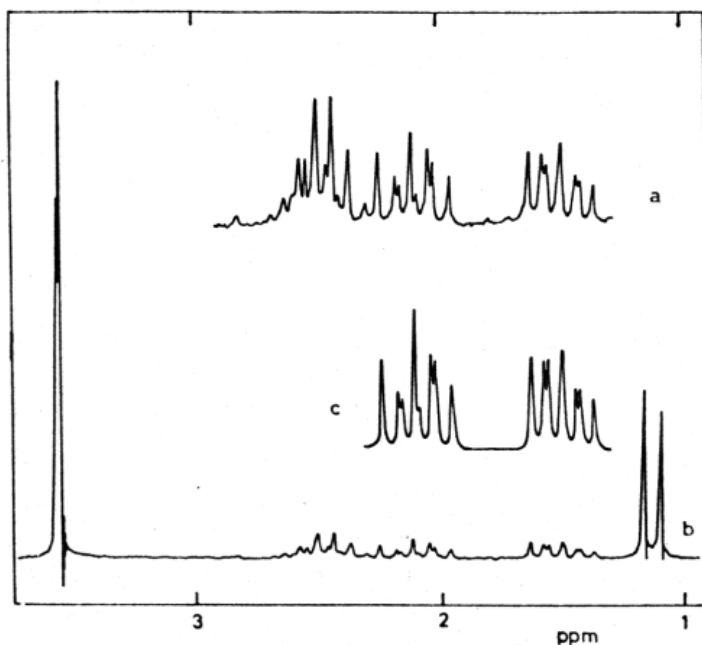


Fig. 4. NMR spectrum, 100 Mc., of iso-MHTC in *o*-dichlorobenzene solution at 26°C. (a), (b) observed; (c) calculated.

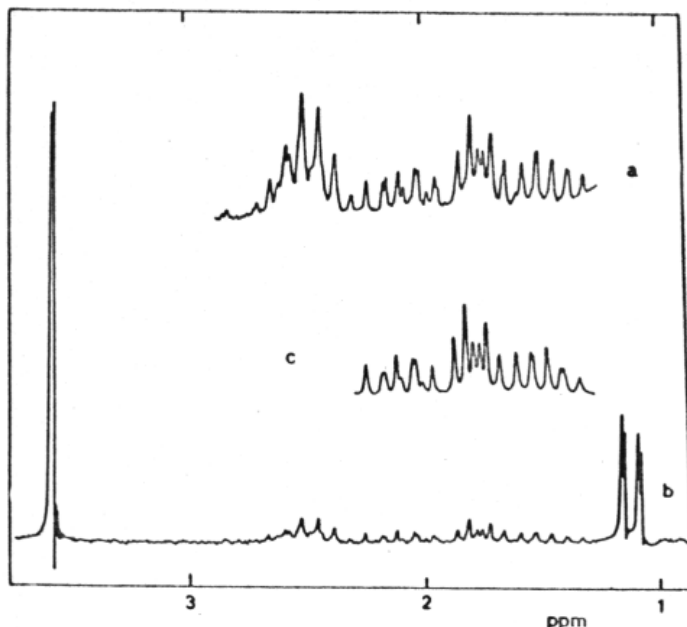


Fig. 5. NMR spectrum, 100 Mc., of hetero-MHTC in *o*-dichlorobenzene solution at 26°C.: (a), (b) observed; (c) calculated.

contribute to affecting shape and width of the respective line. However, the symmetry of the original ABC_2 fragment is disturbed, because the majority of the $F_z(X) F_z(X')$ combinations are unsymmetrical, leading to a collapse of the symmetrical-antisymmetrical 4-spin doublets. We have found that in spectra of the type discussed the peak frequencies and integrated line intensities of the methylene proton band (not, of course, their width and shape) are correctly reproduced by one unsymmetrical 4-spin system ABCD by using for ν_C and ν_D methine proton effective frequencies corresponding to $F_z(X) = +1/2$ and $F_z(X') = -1/2$, respectively (values with highest statistical weight). The theoretical spectrum shown in Figure 2 has been calculated in this way. The methylene proton band of *d,l*-MPDC can in principle be analyzed in a similar way; the "deceptively simple" nature of this spectrum makes, of course, an exact parameter fitting meaningless in our case.

In analogy to the previous argumentation, the methylene proton bands of the three isomers of MHTC (II), representing originally a thirteen-spin problem, can be analyzed and calculated as unsymmetrical seven-spin systems KABLCDM by using the appropriate $\nu_K(x)$ and $\nu_M(x')$ effective frequencies. In syndio-MHTC all the vicinal couplings are so weak ($J/\delta \doteq 0.09$) that a simple four-spin calculation is fully adequate (theoretical "stick" spectrum in Fig. 3), giving identical results with a complete seven-spin calculation. In the iso-MHTC and hetero-MHTC isomers the vicinal interactions are such that the seven-spin calculation has to be applied; their composite theoretical methylene proton bands, calculated with a line-width of 1.2 cps, are shown in Figures 4 and 5. The four-spin and seven-

spin systems were computed by means of a program compiled for the Minsk 22 computer.

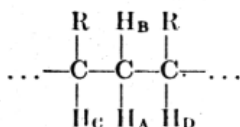
The parameters obtained by analysis of the spectra are summarized in Tables I and II, and the corresponding theoretical spectra are shown in Figures 2 to 5. The chemical shift between methylene protons in isotactic diads is seen to exhibit a similar, although less pronounced, trend to that observed in the vinyl polymer models studied previously:^{1,2} from 0.72 ppm in meso-MPDC it decreases to 0.59 ppm in iso-MHTC, hetero-MHTC exhibiting an intermediate value of 0.63. These values are to be compared with the δ_{AB} shift of 0.44 ppm, determined by Matsuzaki⁷ for isotactic PMA.

On the basis of principles previously established^{1,8,9} the mole fractions and relative energies of the various conformers present may be determined from the values of the vicinal coupling constants, if several limiting as-

TABLE I
NMR Spectral Data at 100 Mc. on Poly(methyl Acrylate) Model
Compounds in *o*-Dichlorobenzene at 26°C.

	Chemical shift, τ				
	X	A	B	C	D
<i>d,l</i> -MPDC ^a	8.94	8.28	8.28	7.57	7.57
Meso-MPDC	8.90	8.61	7.88	7.53	7.53
Syndio-MHTC	8.89	8.31	8.19	7.51	7.43
Iso-MHTC	8.88	8.50	7.91	7.53	7.46
Hetero-MHTC					
s:	8.89	8.31	8.18	7.53	7.45
i:	8.88	8.54	7.91	7.53	7.43
	Spectral parameters, ^b cps				
	J_{AB}	δ_{AB}	d	b'	b
s-diad					
<i>d,l</i> -MPDC ^a	(-13.2)	0	7.1	>-0.8	0
Syndio-MHTC	-13.7	12.3	7.0	-1.9	0
Hetero-MHTC	-13.75	13.4	7.2	-2.5	0
i-diad					
Meso-MPDC	-13.25	72.4	7.4	0	-0.5
Iso-MHTC	-13.8	59.2	7.2	+1.0	-0.8
Hetero-MHTC	-13.65	63.2	7.3	+0.65	-0.5
Isotactic PMA, 140°C. (Matsuzaki)	-13.6	44.3	6.4	—	-0.6

^aMeasured at 60 Mc. and 20°C.:



^b Here $d = 1/4(J_{AC} + J_{AD} + J_{BC} + J_{BD})$, $b' = 1/4(J_{AC} - J_{AD} - J_{BC} + J_{BD})$
 $b = 1/4(J_{AC} + J_{AD} - J_{BC} - J_{BD})$.

assumptions are made: (1) only pure staggered conformational forms are considered, excluding angle distortions, (2) the number of conformers considered is limited by excluding all the forms involving severe steric overlap,

TABLE II
Variation of Vicinal Coupling Constants in Models of Syndiotactic PMA^a

	Vicinal coupling constants at given solvent temp., °C.				
	CCl ₄		o-Dichlorobenzene		
	20°C.	70°C.	20°C.	90°C.	140°C.
<i>d,l</i> -MPDC					
<i>d</i>	7.5	7.2	7.4	7.1	—
<i>b'</i>	-1.9	-1.2	>-0.8	>-0.8	—
Syndio-MHTC					
<i>d</i>	7.4	7.0	7.1	7.0	6.9
<i>b'</i>	-1.8	-1.6	-1.9	-1.7	-1.7

^a Measured at 60 Mc.

TABLE III
Stable Conformations of PMA Models in o-Dichlorobenzene at 26°C.

Isomer (chain config.)	Chain conform.	Reln. mole fraction and coupling data	Equil. ^a compn. <i>x_i</i>	$\Delta E = -RT$ $\ln(x_i/x_0)$, kcal./mole, at 300°K.
<i>d,l</i> -MPDC (s)	TT	$x_1 = 1/2 + b'/(J_T - J_G) = x_0$	<0.60	0
	GG	$x_2 = 1/2 - b'/(J_T - J_G)$	>0.40	<+0.250
meso-MPDC (i)	TG	$x_1 = x_2 = x_0$	1.00	0
	GT			
syndio-MHTC (ss)	TTTT	$x_1 = 2b'/(J_T - J_G) = x_0$	0.38	0
	GGTT			
		$x_2 = x_3$	0.62	+0.120
hetero-MHTC (si)	TTGG			
	TTTG	$x_1 = (b's + b'i)/(J_T - J_G)$ $= x_0$	0.32	0
	TTGT	$x_2 = 1/2 - b'i/(J_T - J_G)$	0.43	-0.200
	GGTG	$x_3 = 1/2 - b's/(J_T - J_G)$	0.25	+0.150
iso-MHTC (ii)	TGTG	$x_1 = x_2 = x_0$	0.80	0
	GTGT			
	GTTG	$x_3 = 2b'/(J_T - J_G)$	0.20	+0.400

^a Calculated for $J_T - J_G = 10$.

and (3) only two fixed values of the *trans* and *gauche* coupling constants J_T and J_G , equal in all the conformers, are used. In addition the value of $J_T - J_G$ must be known.

In the present communication the mole fractions and relative energies of the poly(methyl acrylate) models were calculated by using the relations summarized in Table III and the value of $J_T - J_G = 10$, as established in poly(vinyl chloride)¹⁰ and polystyrene⁸ pentane models. All the PMA models investigated are characterized by a small energy difference between the TT and GG conformational structures of syndiotactic diads. This behavior is in sharp contrast to that observed in the poly(vinyl chloride)¹ and poly(vinyl acetate) models² studied previously. It resembles somewhat the behavior of the two-unit model of syndiotactic polystyrene studied by Bovey,⁸ with a $\Delta E_{290} = +0.70$ kcal./mole; however, it differs from it by the relative temperature independence of the coupling parameter b' (Table II), indicating a small value of the entropic factor ΔS in the syndiotactic PMA models.

As in other vinyl polymer models investigated, all isotactic diads are expected to exist in the TG and GT conformations, corresponding to a segment of the right-handed or left-handed threefold helical arrangement. In iso-MHTC a considerable amount of the GTTG conformation, corresponding to a transition point between the right-handed and left-handed helices, is found. The amount of the GTTG form present is comparable to that found in isotactic 2,4,6-trichloroheptane. All other forms of the isotactic configuration are expected to be excluded on steric grounds.

If all the previously mentioned assumptions were strictly valid, the value of b in Table I should be zero. However, a small nonzero value of this parameter is observed both in PMA models and in the polymer,^{7,11} as well as in most other vinyl polymer models investigated so far.^{1,2} In some cases, e.g., in models of PVC, this discrepancy could at least partly be accounted for by the effect of the orientation of electronegative substituents upon values of vicinal coupling constants.¹² In general, however, some of the above-mentioned basic assumptions have to be regarded as only approximate, and methods have to be sought of determining the extent of deviations.

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