then available, that the dissolution temperatures of these high-pressure crystals were essentially the same as those of higher molecular weight samples crystallized in the conventional manner. As is indicated in Table I, this observation is given further substantiation by the dissolution data for the diversity of solvents that has now been studied. Examination of the pertinent data in the table indicates no difference, within the experimental error, for the dissolution temperatures of the two types of crystalline systems. Similar agreement is obtained when the solubility temperatures for crystalline unfractionated Marlex-50 are compared.[30]

The crystallite thickness of the higher molecular weight conventionally crystallized material is the order of 1000 CH_2 units.[5] If these facts are accepted then the only way that the identical dissolution temperatures (melting temperatures) can be explained is for σ_{ec} of the extended chain, high pressure crystals to be twenty times greater than the conventionally crystallized specimens. This conclusion is reached without the necessity of assigning a value to $T_m°$.[28] Such an extraordinarily high interfacial free energy for extended chain crystals is physically incomprehensible. The problem can be looked upon in another way in that the difference between $T_s°$ as calculated and listed in Table II, and the dissolution temperature for the high-pressure crystals is about 7.5° for all the solvents studied. If it is supposed that the high-pressure crystals represent the equilibrium crystallite and that its solubility temperature can be identified with $T_s°$, as has been assumed,[15,16] then from eq 7 $T_m°$ is found to be 137.2° utilizing the χ_1 value for xylene. This value of $T_m°$ is about 8° below the theoretically calculated values[22] and that experimentally extrapolated.[19] This melting temperature corresponds to that which is conventionally observed experimentally[2,5] so that one would have to conclude that the directly measured melting temperature of a bulk polymer crystallized at atmospheric pressure represents $T_m°$. This conclusion is contrary to a wide array of experimental observation and theoretical analysis.[21] It becomes clear, therefore, that the concept that crystals formed under high pressure are very extended in the chain direction is in need of reexamination.

Conformations of Polyacetaldehyde Model Compounds *via* Dipole Moment Studies and Minimum Potential Energy Calculations[1]

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ABSTRACT: The monomer, dimer (*meso* and racemic) and trimer (isotactic, syndiotactic, and heterotactic) model compounds of polyacetaldehyde were prepared. Their high-resolution nmr spectra were determined and assigned. Dipole moment measurements and minimum potential energy calculations for these compounds (along with calculated dipole moments corresponding to most stable conformations) were carried out. The isotactic trimer model compound was found to have similar internal rotation angles (σ_3^t 125°, σ_4^t 315°) at the potential energy minimum to crystalline isotactic polyacetaldehyde (97.5°, 315°) where the internal rotation angles were deduced from X-ray crystallographic data. The internal rotation angles of syndiotactic (σ_3^t 230°, σ_4^t 25°) and heterotactic (σ_3^t 130°, σ_4^t 340°) trimer model compounds at their potential energy minima cannot be compared to polymeric species since high polymer structural analogs have not been prepared to date.

Since Bovey and his associates[3–5] applied nuclear magnetic resonance to the study of the stereochemistry of polymers, many polymeric systems have had their tacticity analyzed and interpreted by this technique. Model compounds of various polymers have also been examined.[6–9] Their nmr peaks have been related to peaks for respective polymeric analogs. These model compounds generally have known configurations and nmr data can provide conformational information which in turn can be related to the structure of corresponding polymer system.[6–8]

In addition to vinyl polymers, polyaldehydes have also been studied by high-resolution nmr spectros-

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(1) We gratefully acknowledge support for this work by a grant from the National Institutes of Health (Grant GM 08974).

(2) Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

(3) F. A. Bovey, G. V. D. Tiers, and G. Filipovich, *J. Polym. Sci.*, **38**, 73 (1959).

(4) F. A. Bovey and G. V. D. Tiers, *ibid.*, **44**, 173 (1960).

(5) F. A. Bovey and G. V. D. Tiers, *Fortschr. Hochpolym. Forsch.*, **3**, 139 (1963).

(6) S. Fujiwara, Y. Fujiwara, K. Fujii, and T. Fukuroi, *J. Mol. Spectrosc.*, **19**, 294 (1966).

(7) (a) T. Shimanouchi, M. Tasumi, and Y. Abe, *Makromol. Chem.*, **86**, 43 (1965); (b) Y. Abe, M. Tasumi, T. Shimanouchi, S. Satoh, and R. Chujo, *J. Polym. Sci., Part A-1*, **4**, 1413 (1966); (c) D. Doskocilova, *ibid., Part B-2*, 421 (1964).

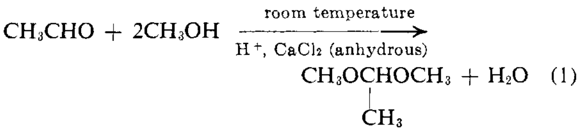
(8) (a) F. A. Bovey, F. P. Hood, III, E. W. Anderson, and L. C. Snyder, *J. Amer. Chem. Soc.*, **42**, 3900 (1965); (b) D. Doskocilova and B. Schneider, *J. Polym. Sci., Part B-3*, 209 (1965).

(9) M. Murano and R. Yamadera, *ibid.*, **5**, 483 (1967).

copy.[10,11] Vicinal couplings in vinyl polymers lead to highly complex splitting patterns which are at best extremely difficult to interpret. These couplings are of course absent in polyaldehydes where the backbone contains alternating carbon and oxygen atoms. Although crystalline isotactic polyacetaldehyde has been studied by X-ray crystallographic methods by Natta and Corradini,[12] it has been impossible to obtain the tacticity of this material in solution by nmr spectroscopy because of its extreme insolubility. On the other hand, "atactic" polyacetaldehyde has been examined extensively by ir and nmr spectroscopy. Results by Vogl,[10] Furukawa,[13] and Goodman[11] have led to a reasonably consistent picture of the tacticity of noncrystalline polyacetaldehydes. It is the purpose of this research to present evidence on the conformations of polyacetaldehyde using model compounds related to a monomeric, a dimeric, and a trimeric form.

These structures can be achieved by preparing and studying the dimethyl acetal of acetaldehyde, the α,α'-dimethoxydiethyl ether (*meso* and racemic) and finally the α,α'-dimethoxydiethyl acetal of acetaldehyde (isotactic, syndiotactic, and heterotactic).

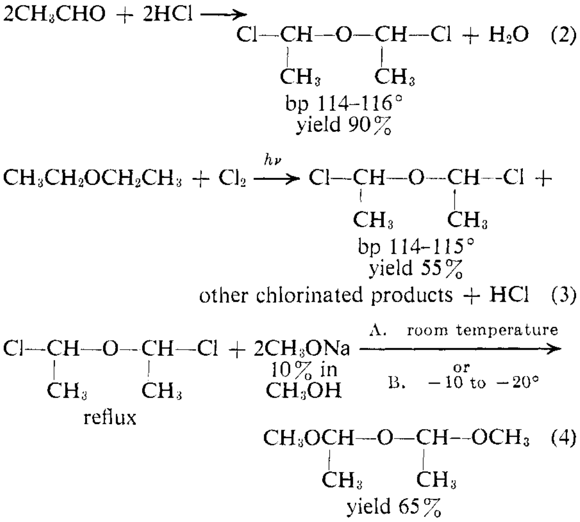
The monomer model compound was obtained by acid-catalyzed acetal formation using methanol and acetaldehyde[14] (eq 1). The dimer model compounds



$$CH_3CHO + 2CH_3OH \xrightarrow[H^+,\ CaCl_2\ (anhydrous)]{room\ temperature} CH_3O\underset{CH_3}{CH}OCH_3 + H_2O \quad (1)$$

are synthesized by methoxylation of α,α'-dichlorodiethyl ether (eq 2–4). Two routes were undertaken to obtain the dichloride. The direct chlorination of diethyl ether followed by fractional distillation as described by Hall and Ubertini[15] gives 55% of α,α'-dichlorodiethyl ether. The other method follows the work of Laatsch[16] involving the dimerization of acetaldehyde in anhydrous hydrogen chloride. Both dichlorides show exactly the same ir, vpc, boiling point, and nmr spectra. This is not surprising, since in both schemes we can propose the intermediate $(CH_2{=}CH_2O^+R)Cl^-$ which tends to equilibrate with the α-chloro ether.[17] Upon methoxylation, both dichlorides give essentially the same distribution of *meso* and racemic model compounds.

SYNTHESES OF ACETALDEHYDE DIMER MODEL COMPOUNDS



$$2CH_3CHO + 2HCl \longrightarrow Cl{-}\underset{CH_3}{CH}{-}O{-}\underset{CH_3}{CH}{-}Cl + H_2O \quad (2)$$

bp 114–116°
yield 90%

$$CH_3CH_2OCH_2CH_3 + Cl_2 \xrightarrow{h\nu} Cl{-}\underset{CH_3}{CH}{-}O{-}\underset{CH_3}{CH}{-}Cl +$$

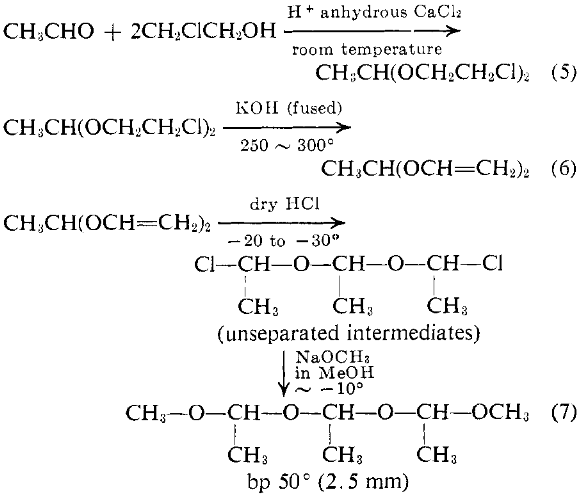
bp 114–115°
yield 55%
other chlorinated products + HCl (3)

$$\underset{reflux}{Cl{-}\underset{CH_3}{CH}{-}O{-}\underset{CH_3}{CH}{-}Cl} + \underset{CH_3OH}{\overset{}{2CH_3ONa}}\ \ 10\%\ in \xrightarrow[B.\ -10\ to\ -20^\circ]{A.\ room\ temperature\ or} CH_3O\underset{CH_3}{CH}{-}O{-}\underset{CH_3}{CH}{-}OCH_3 \quad (4)$$

yield 65%

The trimer model compounds were prepared by methoxylation of α,α'-dichlorodiethyl acetal of acetaldehyde (eq 5–7). The latter is the product of the hydrochlorination of the appropriate divinyl acetal at low temperature. Since the dichloride is so unstable, all attempts to isolate it failed. The divinyl acetal was obtained by dehydrochlorination of the β,β'-dichlorodiethyl acetal of acetaldehyde with fused potassium hydroxide. The acetal was in turn synthesized by acid-catalyzed acetal formation using β-chloroethanol and acetaldehyde.[14]

SYNTHESIS OF ACETALDEHYDE TRIMER MODEL COMPOUNDS



$$CH_3CHO + 2CH_2ClCH_2OH \xrightarrow[room\ temperature]{H^+\ anhydrous\ CaCl_2} CH_3CH(OCH_2CH_2Cl)_2 \quad (5)$$

$$CH_3CH(OCH_2CH_2Cl)_2 \xrightarrow[250\ \sim\ 300^\circ]{KOH\ (fused)} CH_3CH(OCH{=}CH_2)_2 \quad (6)$$

$$CH_3CH(OCH{=}CH_2)_2 \xrightarrow[-20\ to\ -30^\circ]{dry\ HCl} Cl{-}\underset{CH_3}{CH}{-}O{-}\underset{CH_3}{CH}{-}O{-}\underset{CH_3}{CH}{-}Cl$$

(unseparated intermediates)

$$\Big\downarrow {\scriptstyle NaOCH_3\ in\ MeOH\ \sim -10^\circ}$$

$$CH_3{-}O{-}\underset{CH_3}{CH}{-}O{-}\underset{CH_3}{CH}{-}O{-}\underset{CH_3}{CH}{-}OCH_3 \quad (7)$$

bp 50° (2.5 mm)

High-Resolution Nmr Studies of the Model Compounds. Figure 1 contains an nmr spectrum of the dimethyl acetal of acetaldehyde in aniline (~1:3 v/v) at room temperature. As can be seen from Table I, the spectrum consists of one doublet centered at τ 8.84, one singlet at 6.87, and one quartet at 5.63. They are assigned to the absorption of CCH_3 protons, OCH_3 protons, and CH proton, respectively. The integration of proton resonance area bears the proper ratio of 3:6:1. The spin–spin coupling constant is 5.0 ± 0.2 cps (*cf.* Table I).

The nmr spectra for the dimer model compounds (Figure 2) give two sets of doublets centered at τ 8.81

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(10) (a) O. Vogl, *J. Polym. Sci.*, **46**, 261 (1960); (b) E. G. Brame, Jr., and O. Vogl, *J. Macromol. Sci.*, **A1**, 277 (1967).

(11) (a) M. Goodman and J. Brandurp, *J. Polym. Sci., Part A-3*, 327 (1965); (b) J. Brandrup and M. Goodman, *ibid., Part B-2*, 123 (1964).

(12) (a) G. Natta, P. Corradini, and I. W. Bassi, *J. Polym. Sci.*, **51**, 505 (1961); (b) P. Corradini, *J. Macromol. Sci.*, **A1**, 301 (1967).

(13) (a) J. Furukawa and T. Saegusa, "Polymerization of Aldehydes and Oxides," Interscience Publishers, Inc., New York, N. Y., 1963, pp 77–109; (b) H. Fujii, J. Furukawa, and T. Saegusa, *Makromol. Chem.*, **40**, 226 (1960).

(14) (a) A. Adkins and B. H. Nissen, "Organic Syntheses," Coll. Vol. I, A. H. Blatt, Ed., 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1950, p 1; (b) A. Adkins and A. E. Broderick, *J. Amer. Chem. Soc.*, **50**, 178 (1928).

(15) G. E. Hall and F. M. Umbertini, *J. Org. Chem.*, **15**, 715 (1950).

(16) H. Laatsch, *Ann. Chem.*, **218**, 13 (1883).

(17) M. F. Shostakovskii and A. V. Bogdanova, *J. Gen. Chem. USSR*, **17**, 565 (1947).

TABLE I
NMR DATA FOR POLYACETALDEHYDE MODEL COMPOUNDS

	Chemical shift, τ (TMS = 10)		
	$-\overset{\vert}{\underset{\vert}{C}}-H$ (quartet)	OCH_3 (singlet)	CCH_3 (doublet)[a]
Monomer	5.63	6.87	8.84
Isomer I (racemic dimer)	5.33	6.90	8.79
Isomer II (*meso* dimer)	5.44	6.80	8.82
Isomer A (syndiotactic trimer)	5.00, 5.35 (1:2)[b]	6.91	8.67, 8.79 (1:2)[b]
Isomer B (isotactic trimer)	5.29, 5.44 (1:2)[b]	6.80	8.77
Heterotactic trimer	5.09, 5.17, 5.53 (1:1:1)[b]	6.85, 6.89 (1:1)[b]	8.72, 8.79, 8.83 (1:1:1)[b]

[a] Spin-spin coupling constant, J_{AB} = 5.0 ± 0.2 cps. [b] Relative intensities.

and 8.78, two sets of singlets centered at 6.82 and 6.90, and two sets of quartets centered at 5.44 and 5.33. They are assigned to CCH_3, OCH_3, and CH protons, respectively. The integration of proton resonance areas bears the correct ratio of 3:3:1. The spin-spin coupling constant is 5.0 ± 0.2 cps (*cf.* Table I). Since there are no methylene protons in the chain, it is not possible to obtain the configurations of the model compounds from the patterns of the nmr spectrum. The definite assignment of these peaks to the corresponding isomers will be discussed in a later part of this paper.

The nmr spectrum of the trimer model compounds (Figure 3) exhibits overlapping doublets in the region of τ 8.9–8.6, four sharp singlets centered at τ 6.91, 6.89, 6.85, and 6.80, and overlapping quartets in the region of τ 5.5 and 5.0. They are assigned to the CCH_3, OCH_3, and CH protons, respectively. The integration of proton resonance areas bears a ratio of 3:2:1 as should be the case for these compounds. Once again the spin-spin coupling constant is 5.0 ± 0.2 cps (*cf.* Table I).

Analysis of Configurations of Dimer and Trimer Model Compounds by Nmr (Table I). It is interesting that in the region of the proton absorption we are able to relate the frequencies of the resonances to configuration. In the case of the CCH_3 absorptions, the racemic dimer model compound exhibits a doublet at τ 8.79. In addition, the racemic dyad of the syndiotactic trimer model compound also has its absorption at τ 8.79. We therefore conclude that the absorption at τ 8.79 for the heterotactic trimer model compound should be assigned to the contribution of the racemic dyad portion of this molecule. Since the *meso* dimer model compound shows its CCH_3 absorption at τ 8.82, the doublet at 8.83 for the heterotactic trimer model compound can be attributed to the *meso* dyad portion of this molecule. The additional doublet at τ 8.72 must be attributed to the central methyl of the heterotactic triad. On this basis, we designate the central methyl of the syndiotactic triad to be at τ 8.67, and the central methyl of the isotactic triad to be at τ 8.77. In the latter case, we encountered only one CCH_3 doublet. The reason for this is not understood at present.

As for the region for methinyl (CH) proton resonance, we find there is good agreement on one hand between the racemic dimer model compound (τ 5.33) and the racemic dyads of the syndiotactic trimer model com-

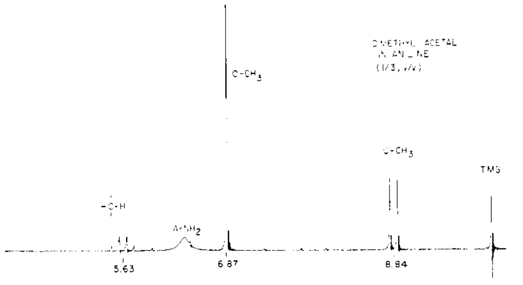

Figure 1. The nmr spectrum of dimethyl acetal of acetaldehyde in aniline (1:3, v/v) at room temperature.

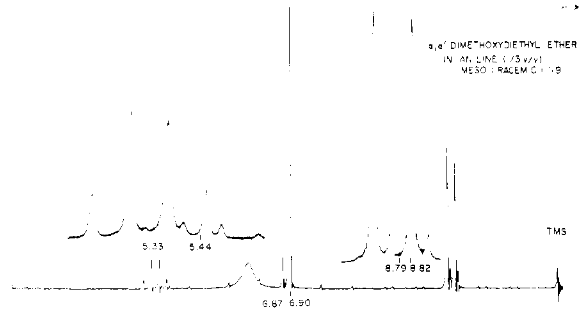

Figure 2. The nmr spectrum of α,α′-dimethoxydiethyl ether in aniline (1:3, v/v) at room temperature.

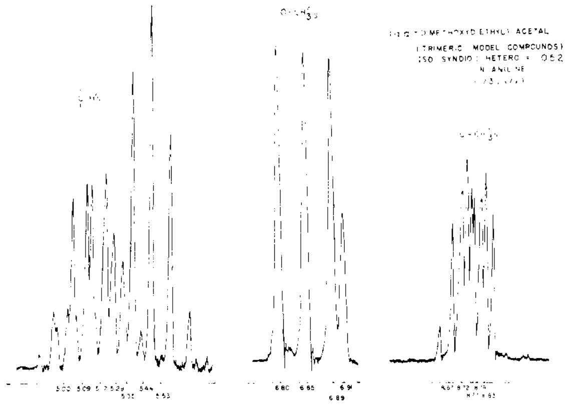

Figure 3. The nmr spectrum of α,α′-dimethoxydiethyl acetal of acetaldehyde in aniline (1:3, v/v) at room temperature. (Note: each region is magnified and extended arbitrarily.)

pound (4.35), and on the other hand, between the *meso* dimer model compound (5.44) and the *meso* dyads of isotactic trimer model compound (5.44). The central methinyl of the syndiotactic triad has an absorption at τ 5.00, while the central methinyl of the isotactic triad exhibits absorption at 5.29. These assignments are consistent with the CCH_3 analysis above. Relative intensities of these peaks also support the structural assignments. The three sets of quartets attributed to the heterotactic trimer model compound can be assigned as a first approximation: τ 5.53 to *meso*, τ 5.17 to racemic dyads, respectively, and the τ 5.09 absorption is therefore designated as arising from the central methinyl heterotactic triad.

In the region of the nmr spectrum for the methoxyl proton resonance, we find good agreement for the frequency arising from the methoxyl in the racemic dimer model compound and the syndiotactic trimer model compound. We also find that the methoxyl of the *meso* dimer model compound exhibits its absorption at the same frequency as the methoxyl of the isotactic trimer model compound. The heterotactic isomer shows two methoxyl resonances at intermediate frequencies τ 6.85 and 6.89. Of course, since the methoxyl groups are end groups only, we cannot expect the heterotactic peaks to be identical with those shown by either syndio- or isotactic trimer model compounds.

Determination of Dipole Moments of the Model Compounds. Guggenheim's simplified method for dipole moment determination in dilute solution[18,19] was employed in this work (eq I) where k = Boltzmann's constant,

$$\mu^2 = \frac{27kT}{4\pi N}\frac{M_2}{d_1(\epsilon_1 + 2)(n_1^2 + 2)}(a - b) \qquad \text{(I)}$$

N = Avogadro's number, d_1 = density of solvent, ϵ_1 = dielectric constant of solvent, n_1 = refractive index of solvent Na D line, a = slope of dielectric constant increment *vs.* weight fraction at infinite dilution, b = slope of square of refractive indices increment *vs.* weight fraction at infinite dilution.

Of the compounds with which we dealt, only the monomer model compound is available in pure form. The dimeric and trimeric forms could not be isolated as pure diastereoisomers. Instead we were able to obtain samples enriched in specific stereoisomers for both the dimer and trimer series by proper use of preparative gas chromatography. As we can see from the equation suggested by Guggenheim,[18] the terms a and b are the determining factors of dipole moment since the remaining part of the equation is the same for each of the diastereoisomeric compounds. Moreover, from a theoretical point of view, factor b is essentially the same for compounds of the same bond types. And even if there were any steric effects to make this assumption invalid, the contribution is negligibly small, as we can see from the actual calculations. It appears from our work that b remains constant for different enriched samples while a shows some changes. Thus the factor a remains the sole parameter in the variation of dipole moment from diastereoisomer to diastereoisomer. Since we do not have pure compounds in the dimeric and trimeric series, we can express a as eq II. Here

$$a_{\text{exp}} = \frac{\Delta\epsilon_{\text{exp}}}{\Delta W_2} = \frac{(C_1\epsilon_{12}{}^{1a} + C_2\epsilon_{12}{}^{2a} + C_3\epsilon_{12}{}^{3a} + \ldots) - (C_1\epsilon_{12}{}^{1b} + C_2\epsilon_{12}{}^{2b} + C_3\epsilon_{12}{}^{3b} + \ldots.)}{(C_1W_2{}^a + C_2W_2{}^a + C_3W_2{}^a + \ldots.) - (C_1W_2{}^b + C_2W_2{}^b + C_3W_3{}^b + \ldots.)} \qquad \text{(II)}$$

$C_1, C_2, C_3\ldots$ denote the fractions of each isomer in any given sample (for this reason $C_{\text{total}} = C_1 + C_2 + C_3 + \ldots = 1.0$); $\epsilon_{12}{}^{1a}$ denotes the dielectric constant of the solution for isomer 1 at a concentration a, $\epsilon_{12}{}^{2a}$ for isomer 2 at the same concentration, and so on; $\epsilon_{12}{}^{1b}$, in turn, denotes the dielectric constant of isomer 1 at a concentration b, etc; $W_2{}^a$ denotes the combined weight fraction of a given sample at a concentration a, while $W_2{}^b$ represents the same at a concentration b. Let $\Delta\epsilon_{12}{}^1 = \epsilon_{12}{}^{1a} - \epsilon_{12}{}^{1b}$, which is the difference of dielectric constants for isomer 1 at two different concentrations, $\Delta W_2 = W_2{}^a - W_2{}^b$, which is the difference of combined weight fractions at two concentrations a and b. From this elucidation we are able to formulate eq III. Here $a^1, a^2, a^3\ldots$ denote the values of a for isomers 1, 2, 3,..., respectively, in eq I.

$$a_{\text{exptl}} = \frac{C_1\Delta\epsilon_{12}{}^1 + C_2\Delta\epsilon_{12}{}^2 + C_3\Delta\epsilon_{12}{}^3 + \ldots}{\Delta W_2} = C_1a^1 + C_2a^2 + C_3a^3 + \ldots \qquad \text{(III)}$$

Four different dimer and five different trimer samples were investigated. Each sample was studied at five concentrations (in the range from 0.2 to 4% w/w). We were able to calculate $a^1, a^2, a^3\ldots$ by solving the appropriate simultaneous equations. We measured the distribution of isomer I and II of the dimer mixture by the intensities of the nmr peaks at τ 6.91 and 6.80, respectively. From these data we obtained the value of a and thus the experimental values of the dipole moment for each isomer. These were listed in Table II. In a similar manner we ascertained the amounts of trimers A and B and the heterotactic trimer.[20]

In our measured value for the dipole moment we found that the solvent effects are small. These model compounds give somewhat larger observed dipole moments in benzene than in hexane.

Eyring[21] suggested that the resultant electric moment of a chain molecule can be calculated for different conformations if the direction and magnitude of the electric moments are well defined by using a transformation matrix. Shimanouchi and Mizushima[22] developed the matrix operation for helical macromolecules. We extended the above ideas by employing bond moments for computation of resultant dipole moments. The bond moments are designated $\bar{\mu}_{CH_2-O}$ = 1.10 D and

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(18) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

(19) J. W. Smith, *ibid.*, **46**, 394 (1950).

(20) We could assign the heterotactic structure to one of the trimeric compounds on the basis that there is a clear doublet in the methoxyl region associated with this isomer which lies between singlets for isomers A and B. We, of course, are unable to assign proper tacticity to isomers A and B. In a later section of this manuscript we demonstrate how we decide on the configurations of these two substances.

(21) H. Eyring, *Phys. Rev.*, **39**, 746 (1932).

(22) T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **23**, 707 (1955).

TABLE II

CALCULATED AND MEASURED DIPOLE MOMENTS FOR THE MODEL COMPOUNDS

Model compounds	—Experimental, D— *n*-Hexane (20°)	Benzene (25°)	Calcd, D
Monomer	1.64	1.65	1.96
Dimer			
Isomer I (racemic)	1.77	1.77	1.46
Isomer II (*meso*)	2.45[a]	2.49[a]	2.30
Trimer			
Isomer A syndiotactic	1.22[a]	1.28[a]	2.60[b]
Isomer B isotactic	2.85[a]	2.90[a]	3.05
Heterotactic	2.11[a]	2.16[a]	1.95

[a] All of these values are obtained by utilization of eq I–III. [b] The syndiotactic trimer exhibits a much lower value for its dipole moment than we calculated. This may arise from the high degree of flexibility for the molecule, as can be seen from the contour map, Figure 11

TABLE III

VAN DER WAALS INTERACTION FUNCTIONS

H···H[a]	$3.7164 \times 10^3 \exp(-3.0708r) - 89.52r^{-6}$ [f]
$CH_3\cdots CH_3$[b]	$2.39 \times 10^4 r^{-7.37}$ ($r \leq 3.20$ Å) $2.739 \times 10^5 \exp(-3.329r) - 2.942 \times 10^3 r^{-6}$ ($r > 3.20$ Å)
C···C[c]	$3.012 \times 10^5 r^{-12} - 327.20r^{-6}$
O···O[d]	$1.45 \times 10^5 r^{-12} - 367r^{-6}$
C···H[e]	$[3.347 \times 10^4 \exp(-1.5354r) - 589.0]r^{-6}$
$C\cdots CH_3$[e]	$[2.879 \times 10^5 \exp(-1.6645r) - 1235]r^{-6}$
$H\cdots CH_3$[e]	$3.1905 \times 10^4 \exp(-3.1999r) - 1702r^{-6}$
O···H[e]	$1.982 \times 10^4 \exp(-3.8395r) - 497.61r^{-6}$
O···C[e]	$[1.785 \times 10^5 \exp(-2.304r) - 202.2]r^{-6}$
$O\cdots CH_3$[e]	$1.919 \times 10^5 \exp(-3.959r) - 1044r^{-6}$

Bond Angles

COC 110°	CCO 110°	HCO 109°

Bond Lengths

C–H 1.00	C–C 1.53	C–O 1.43

[a] J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.*, **18**, 130 (1950). [b] E. A. Mason and M. M. Kreevoy, *J. Amer. Chem. Soc.*, **77**, 5808 (1955). [c] L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960). [d] R. A. Scott and H. A. Scheraga, *ibid.*, **45**, 2091 (1966). [e] These interaction functions [P. De Santis, E. Giglio, A. M. Liquori, and A. Ripamonti, *J. Polym. Sci., Part A-1*, 1383 (1963)] are minimized by using the following values of van der Waals radii: R_H 1.20 Å; R_C 1.70 Å; R_O 1.35 Å; R_{CH_3} 2.00 Å. [f] The values for r are in angstroms and energies are noted in kilocalories per atom pair.

$\vec{\mu}_{CH-O} = 0.99$ D. These values are obtained respectively from the dipole moments of dimethyl ether ($\mu = 1.31$ D)[23] and diethyl ether ($\mu = 1.21$ D).[24a] We set the value for $\vec{\mu}_{CH_3-C}$ and $\vec{\mu}_{CH-C}$ equal to zero in our calculations[24b] and consider that bond moments lie along the covalent bonds. We computed dipole moments for the various rotational states of these model compounds (Table II) and ascertained that a rotation of 10° from the potential energy minimum (see next section) leads at most to a 15% change in the value of the calculated dipole moments.

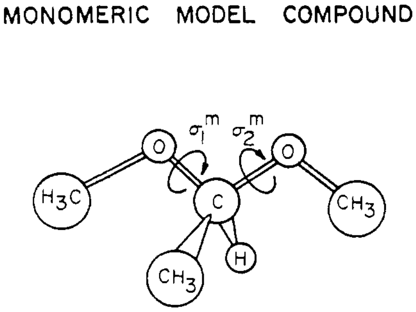

Figure 4. Stereochemical view of the monomer model compound of acetaldehyde where $\sigma_1^m = \sigma_2^m = 0°$.

Calculation of the Conformational Potential Energy for the Model Compounds. The conformational potential energy of each molecule was calculated by summing all the "intramolecular" atomic and/or group interactions. The total energy corresponding to a specific rotational state can be expressed as

$$U(\sigma_i) = {}^1/_2U_0(1 - \cos 3\sigma_i) + [a_k \exp(-b_k r_k) - c_k r_k^6 - \epsilon_k/r_k]$$

where U_0 denotes the rotational energy barrier (following the suggestion of Scheraga[25] it is taken as 1.07 kcal/mol for the C–O bond); σ_i refers to the internal rotational angles which are set equal to zero degrees for a fully extended chain (*i.e.*, all C–O bonds are *trans* to each other); the subscript i denotes rotational states; a, b, and c represent the coefficients to the van der Waals interaction functions for the corresponding atomic pairs (Table III); r refers to the distances between pairs of atoms and/or groups; and ϵ_k denotes the electrostatic contribution term. In our calculation, we follow the suggestion of Flory and Brandt[26a] and use partial charges rather than dipole–dipole interactions. The dielectric constant of the medium is set at 4.0, since the data for various ethers exhibit values between 3.5 and 4.5 at room temperature.[26b] The partial charges are evaluated on the basis of the bond moments and lengths for the interaction pair under consideration.

A program was written for the IBM system 360 computer in Fortran IV to calculate the interactions as a function of rotational angles. The total conformational energy is thus obtained for corresponding rotational states.

In the case of the monomer model compound, there are two rotational internal angles σ_1^m and σ_2^m (Figure 4).[27] We constructed a two-dimensional plot of conformational potential energy from the numerical data calculated by rotating σ_1^m and σ_2^m at intervals of 10° each. When we encountered energy minima, we calculated total energy at 2° intervals. The rotational angles σ_1^m and σ_2^m in Figure 5 correspond to 360° rotations of each and show the locations of minimum potential energy states. The absolute value at the deepest

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(23) U. Blukis, P. H. Kasal, and R. J. Myers, *J. Chem. Phys.*, **38**, 2753 (1963).

(24) (a) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, 1963; (b) J. E. Mark and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 3705 (1966).

(25) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **42**, 2209 (1965).

(26) (a) P. J. Flory and D. A. Brandt, *J. Amer. Chem. Soc.*, **87**, 663 (1965); *ibid.*, **87**, 2791 (1965); (b) C. D. Hodgman, "Handbook of Chemistry and Physics," 44th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1963, p 2613.

(27) We designate all internal rotational angles by the symbol σ. We differentiate those for monomer, dimer, and trimer by superscripts m, d, and t, respectively. All internal rotation angles are obtained by clockwise rotations.

TABLE IV
INTERNAL ANGLES OF THE ROTATION AT THE DEEPEST POTENTIAL ENERGY MINIMA

Internal rotation angles	—Dimeric model compounds— *meso*	racemic
σ_1^d	120	120
σ_2^d	335	340
σ_3^d	125	340
σ_4^d	320	120

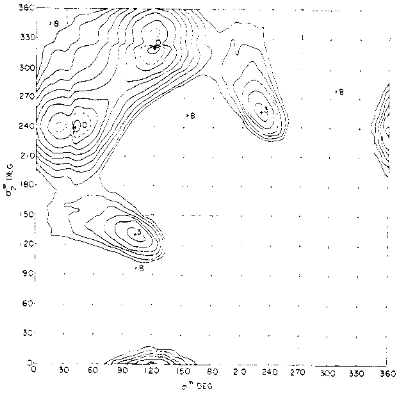

Figure 5. Conformational contour energy map of the monomer model compound of acetaldehyde; internal energy of dimethyl acetal (kilocalories per mole).

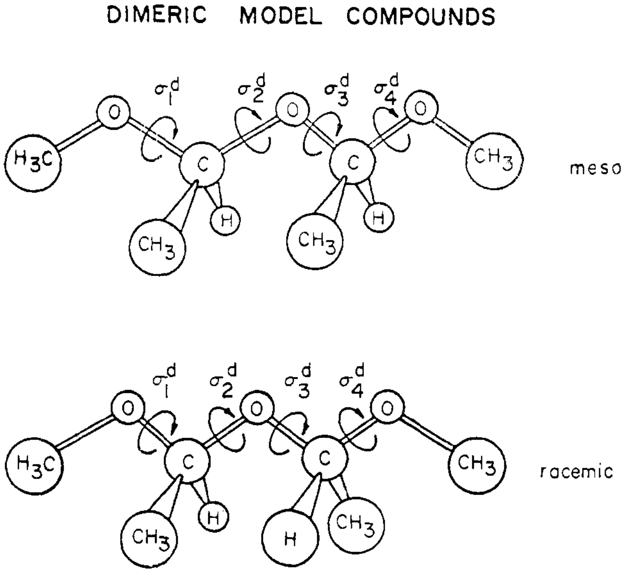

Figure 6. Stereochemical view of the dimer model compounds of acetaldehyde where $\sigma_1^d = \sigma_2^d = \sigma_3^d = \sigma_4^d = 0°$.

minimum potential energy well is 11.4 kcal/mol, but it is arbitrarily set equal to zero. The structure in Figure 5 results from rotations of σ_1^m and σ_2^m of 40 and 240°, respectively. The enantiomeric structure is arrived at by rotations of σ_1^m and σ_2^m of 120 and 320°, respectively. The conformers lead essentially to a *trans–gauche* structure, but with σ_1^m (or σ_2^m for enantiomer) twisted 40° from the normal *trans*-staggered position. The internal rotation angles σ_1^m and σ_2^m, corresponding to the next higher energy minimum (about 3 kcal/mol higher), occur at σ_1^m 104° and σ_2^m 130°. The enantiomeric structure shows its minima at σ_1^m 230° and σ_2^m 256°. These conformers represent *gauche–gauche* structures with deviations of 16 and 10° from the normal *gauche–gauche* positions.

For the *meso* and racemic dimer model compounds there are four internal rotation angles as shown in Figure 6. In order to calculate the mimimum potential energies we allow these angles to rotate through 360° at 60° intervals. In this manner we are able to rule out many conformations on the basis that these structures are impossible or exhibit substantially higher potential energies than other conformers. The allowed regions of rotation are then examined using 30° intervals of rotations for σ_1^d, σ_2^d σ_3^d, and σ_4^d. By the same criteria as above, we can eliminate additional structures. We extend this procedure to consecutive steps of 20, 10, and 5° intervals of rotations. Of course, each subsequent refinement of the calculation is applied only to those allowed regions of internal rotations remaining from the previous step.

Table IV contains the results showing the internal rotational angles corresponding to the minimum potential energy of the *meso* and racemic dimer model compound.

We observed that σ_1^d and σ_4^d are identical with the internal rotation angles (σ_1^m and σ_2^m) for the monomer model compound at the point of minimum potential energy. We therefore can set the values of σ_1^d and σ_4^d for both the *meso* and racemic model compounds and allow σ_2^d and σ_3^d to rotate through 360°. Using this approach, we construct energy contour maps for both dimer model compounds (Figures 7 and 8). The *meso* compound (σ_1^d 120°, σ_4^d 320°) exhibits the deepest potential energy minimum at σ_2^d 335° and σ_3^d 125°. The racemic compound (σ_1^d, σ_4^d 120°) shows its minimum at σ_2^d, σ_3^d 340°. These values are identical with those obtained above by sequential rotational refinements applied to all four angles. From the contour maps we calculate the energy values at the deepest minima to be 9.5 kcal/mol for the *meso* and 8.9 kcal/mol for the racemic compounds. In the figures we arbitrarily set these values equal to zero. The magnitude of the potential energy minima may be off by 0.5–1.5 kcal/mol depending on the steepness of the energy contour since each internal angle can be rotated ±10° without materially affecting the positions of the energy minima.

For the dimer model compounds, we described two approaches to obtain the structure of the most stable conformers. When we deal with the trimeric model compounds (Figure 9), we encounter six internal rotational angles for each isomer. In these cases we must apply the fact that σ_1^t and σ_6^t are identical with the corresponding σ_1^d and σ_4^d. Thus, for the isotactic trimeric model compound, σ_1^t and σ_6^t can be set equal to σ_1^d and σ_4^d (*meso*), *i.e.*, 120 and 320°, respectively. At this point we allow the remaining four internal angles to rotate as described above for the dimeric model compounds. Table V contains a summary of the internal rotational angles for the deepest potential energy minimum.

The most stable conformation of the syndiotactic trimer model compound is obtained by employing the relationship between the values of σ_1^t and σ_6^t, and racemic σ_1^d and σ_4^d. If σ_1^d and σ_1^t are both set at 120°, then σ_4^d and σ_6^t become 120 and 240°, respectively, in order

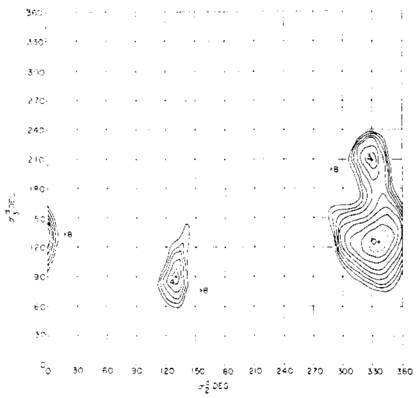

Figure 7. Conformational contour energy map of the *meso* dimer model compound of acetaldehyde where $\sigma_1^d = 120°$, $\sigma_4^d = 320°$; internal energy of *m*-α,α'-dimethoxydiethy ether (kilocalories per mole).

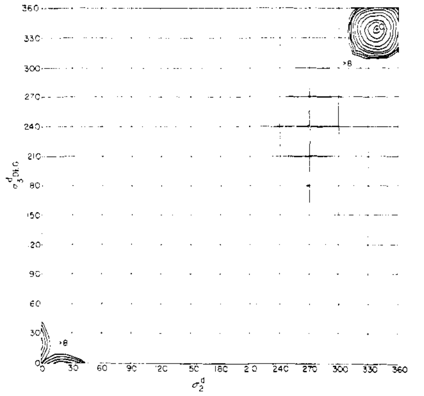

Figure 8. Conformational contour energy map of the racemic dimer model compound of acetaldehyde where $\sigma_1^d = \sigma_4^d = 120°$; internal energy of racemic α,α'-dimethoxydiethyl ether (kilocalories per mole).

to maintain a consistent stereochemical relationship between dimer and trimer model compounds. As with the *meso* analog above, we allow the other four internal angles to rotate. Table V shows the angles required to locate the minimum potential energy.

For the heterotactic model compound, we set σ_1^t and σ_6^t equal to the values of σ_1^d for the *meso* and σ_4^d for the racemic dimer model compounds (*i.e.*, 120° for both). Once again the other four internal angles are allowed to rotate to locate the potential energy minima. Table V shows the angles for the deepest minimum.

The values of σ_3^t and σ_4^t are related to the internal rotational angles for the high polymer. Thus we are concerned with comparisons of these angles with data from stereoregular high molecular weight samples of polyacetaldehyde. We, therefore, set the values of σ_1^t, σ_2^t, σ_5^t, and σ_6^t for each of the trimeric model compounds and allowed σ_3^t and σ_4^t to rotate over 360° and carefully established potential minima and contour maps which are shown in Figures 10, 11, and 12.

Discussion

We were able to use dipole moments to establish firmly the configurations of the dimer and trimer model compounds. These results are fully consistent with our tentative configurational assignments based on nmr analysis.

TABLE V

INTERNAL ANGLES OF ROTATION AT THE DEEPEST POTENTIAL ENERGY MINIMA FOR TRIMERIC MODEL COMPOUNDS

Internal rotation angles	Angle, deg		
	Isotactic	Syndiotactic	Heterotactic
σ_1^t	120	120	120
σ_2^t	340	340	340
σ_3^t	125	230	130
σ_4^t	315	25	340
σ_5^t	120	20	340
σ_6^t	320	240	120

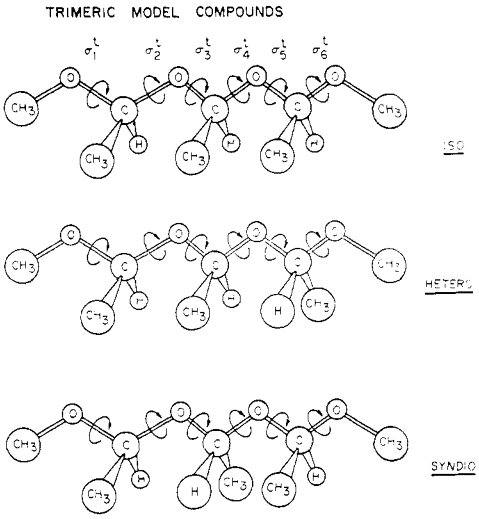

Figure 9. Stereochemical view of the trimer model compounds of acetaldehyde where $\sigma_1^t = \sigma_2^t = \sigma_3^t = \sigma_4^t = \sigma_5^t = \sigma_6^t = 0°$.

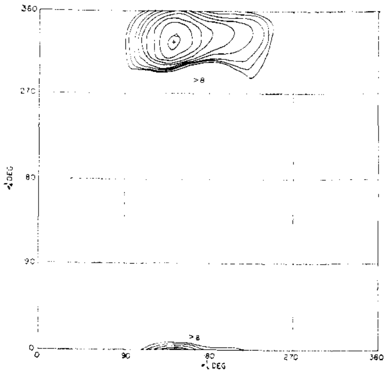

Figure 10. Conformational contour energy map (kilocalories per mole) of the isotactic trimer model compound of acetaldehyde (polyacetaldehyde) under the conditions that $\sigma_1^t = 120°$, $\sigma_2^t = 340°$, $\sigma_5^t = 120°$, and $\sigma_6^t = 320°$.

The observed dipole moment of the monomeric model compounds is 1.64 D which is lower than the calculated value (1.96 D) for this molecule at its miminum potential energy (σ_1^m 40°, σ_2^m 240°). The experimental value is much larger than that calculated for this molecule at the next higher minimum potential energy (σ_1^m 104°, σ_2^m 130° [0.36]. This energy well is about 3 kcal/mol higher than the "twisted *trans–gauche*" state above and corresponds to a "*gauche–gauche*" state. From these observations we conclude that about 20% *gauche–*

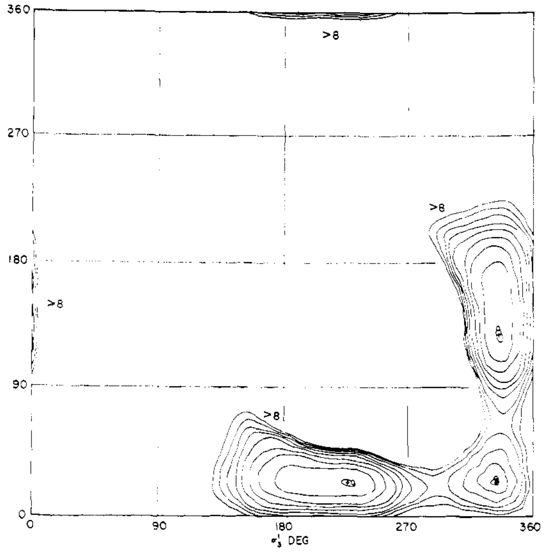

Figure 11. Conformational contour energy map (kilocalories per mole) of the syndiotactic trimer model compound of acetaldehyde (polyacetaldehyde) under the conditions that $\sigma_1^t = 120°$, $\sigma_2^t = 340°$, $\sigma_5^t = 20°$, and $\sigma_6^t = 240°$.

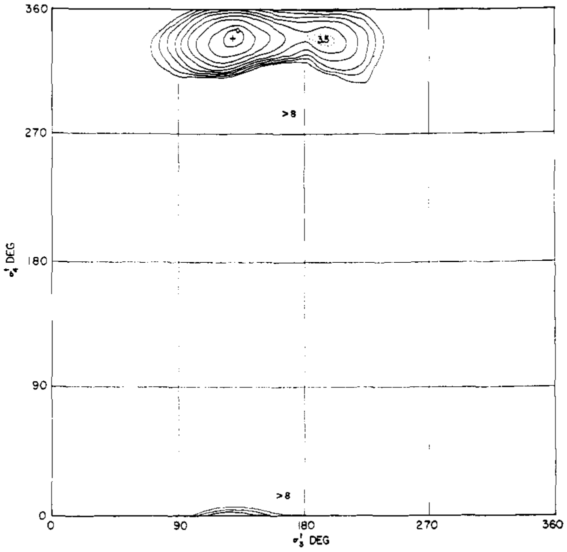

Figure 12. Conformational contour energy map (kilocalories per mole) of the heterotactic trimer model compound of acetaldehyde (polyacetaldehyde) under the condition that $\sigma_1^t = 120°$, $\sigma_2^t = 340°$, $\sigma_5^t = 340°$, and $\sigma_6^t = 120°$.

gauche conformers exist at room temperature. This contribution is based on the assumption that only two conformers of lowest potential energy occur at room temperature. At this time we must point out that we used hard sphere potentials for $CH_3 \cdot \cdot \cdot CH_3$ interactions.[28] We expect that the actual energy barrier between conformers is lower than we calculated since the CH_3 groups can slide past each other by suitable rotations of CH_3 groups to the position of minimum $H \cdot \cdot \cdot H$ contact. We were unable to treat methyl groups in the more complete manner because of the increase in the complexity of the calculations of minimum potential energy. However, we are able to state that our treatment is quite sufficient to describe the most stable rotational isomers for the monomer, dimer, and trimer model compounds.

Isomer I exhibits a dipole moment of 1.77 D for the pure form in benzene while the racemic dimer model compound leads to a calculated value for the dipole moment of 1.46 D. Isomer II gives a dipole moment of 2.49 D while the *meso* structures lead to a calculated value for the dipole moment of 2.30 D. As a result we conclude that isomer I is the racemic and isomer II is the *meso* dimer model compound.

We could obtain the value for the dipole moment of the heterotactic model compound, since the nmr spectra allow us clearly to identify the peaks associated with this isomer. Using eq I–III, we computed the experimental value for the heterotactic trimer—2.16 D. From the structure at the potential energy minimum, we calculated the dipole moment to be 1.95 D. On a basis similar to our assignments in the dimer model compound series, we designated isomer A ($\mu = 1.22$ D) to be syndiotactic trimer compound for which we calculate the dipole moment to be 2.60 D. Isomer B is assigned the isotactic structure ($\mu = 2.90$ D). On the basis of the potential energy minimum, we calculate the dipole moment of the isotactic trimer model compound to be 3.05 D.

As noted above, we can compare our data with the X-ray diffraction analysis on crystalline isotactic high molecular polyacetaldehyde. Natta and Corradini[12] found this polymer to be constructed of a left-handed helix with internal rotation angles of 97.5 and 315°[29] (or a right-handed helix with internal rotation angles of 262.5 and 45°). The agreement between the internal rotation angles of the model compound and high polymer are reasonably good (*i.e.*, the differences in the two are 27.5 and 10°). It appears that the isotactic trimer model compound exhibits a more compact helical structure than does the high polymer in the crystalline state. It is not surprising that the long-range interactions for crystalline polymer of infinitive chain length causes the helix to extend itself. In line with this reasoning we can cite the work of Borisova and Birshtein,[30] who calculated that the internal rotation angles should be 100 and 330° for isotactic polyacetaldehyde of infinitive chain length. These values are extremely close to σ_3^t and σ_4^t for our isotactic trimer model compound.

As for syndiotactic and heterotactic trimer model compounds, the internal angles of rotation (σ_3^t and σ_4^t) have no counterpart in the polymer domain since these polymeric analogs have not been prepared.

Experimental Section

All boiling points are uncorrected. Nuclear magnetic resonance (nmr) spectra were determined with a Varian Model A-60 spectrometer, and resonances are expressed in units relative to tetramethylsilane as the internal standard. The peak areas are measured by a Maho-Compensation Planimeter (Henschel Co., New York, N. Y.). An Aeroprep Model 700-A vapor phase chromatograph (Wilkens

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[28] See Table II, footnote *b*.

[29] According to the Natta–Corradini notation and convention for rotation the values for the angles are σ_2 82.5°, σ_1 225°. These are the analogs to σ_3^t 97.5°, σ_4^t 315°, respectively, for the isotactic trimer model compound.

[30] N. P. Borisova and T. M. Birshtein, *Polym. Sci. USSR*, **4**, 907 (1963).

Instrument Co.) with a $^3/_8$ in. × 20 ft column (solid support, HMDS Chromosorb A.W. 60/80; stationary phase, 20% Carbowax 400) was employed for the fractionation of the dimeric and trimeric model compounds. Dielectric constants were determined with a dipolemeter, Type DM 01 (Kahl Scientific Instrument Co.), using benzene or *n*-hexane solutions. Refractive indices were determined by a dipping refractometer (Zeis Optics Co.). Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, N. Y.

Purification of Solvents and Starting Materials. Solvent grade *n*-hexane was purified by the method of Morgan and Lowry:[31] bp 69.0°; d_4^{20} 0.6697; $n^{20}\mathrm{D}$ 1.37919; ϵ^{20} 1.9075 (lit.[31] bp 65–70°, d_4^{20} 0.6775, $n^{20}\mathrm{D}$ 1.378, ϵ^{20} 1.910). Benzene (99 mol % pure, Fisher Scientific Co., Inc.) was dried by passing through fresh Molecular Sieves (Type 4A, Linde Air Products Co.) in an anhydrous atmosphere.

Commercial acetaldehyde (Eastman Chemical Co.) was stored over molecular sieves and distilled from Age Rite White (R. T. Vanderbilt Co., Inc., trade name for *sym*-2-naphthalene-*p*-phenylenediamine) which served as an antioxidant, bp 20–21°. The dimethyl acetal was prepared according to the method of Adkins and Nissen,[14] which was further distilled over sodium in a dry atmosphere. All other materials were reagent grade, and were used without further purification.

α,α′-Dichlorodiethyl Ether. A. From the Dimerization of Acetaldehyde. Anhydrous hydrogen chloride gas (182 g, 5.0 mol) was passed into acetaldehyde (200 g, 4.5 mol) at −10 to −20°. The reaction mixture was then cooled to −40° and kept at this temperature until all of the water formed during the reaction had crystallized out of the solution. Rapid filtration at −40° removed most of the ice, the filtrate was then allowed to stand over anhydrous calcium chloride for 1 hr. After removing the calcium chloride by filtration, α,α′-dichlorodiethyl ether (272 g, 85%) was obtained by distillation: bp 113–115° (lit.[16] bp 116–117°; $n^{25}\mathrm{D}$ 1.4175; nmr (neat) doublet centered at τ 8.28 (J = 5.0 ± 0.2 cps), quartet, centered at 6.09 (J = 5.0 ± 0.2 cps). The peak areas of the nmr spectrum had a ratio of 3:1 and were assigned to the methyl proton and methinyl proton resonance, respectively. The product showed a single peak under vpc analysis (inert columns).

B. From the Photochlorination of Diethyl Ether.[15] Anhydrous chlorine gas (178 g, 2.5 mol) was slowly bubbled into anhydrous ether (150 g, 2.0 mol in a 1-l. three-necked, Vycor glass flask), while the system was irradiated at −20 to −30° with the uv light from a low-pressure mercury lamp. The system was kept anhydrous throughout the reaction. After the addition was completed, the reaction mixture was distilled. The fraction boiling at 100–120° was collected and redistilled through a 2-ft column packed with glass helices. The fraction (129 g, 45%) boiling at 113–115°, $n^{20}\mathrm{D}$ 1.4179 (lit.[15] bp 113–114°, $n^{20}\mathrm{D}$ 1.4183), was shown to be identical with the product from preparation A.

α,α′-Dimethoxydiethyl Ether. Freshly cut sodium (35 g, 1.5 mol) was completely dissolved in 350 ml of absolute methanol. To this clear solution, α,α′-dichlorodiethyl ether (90 g, 0.63 mol) was slowly added with stirring at −10 to −20°.[32] The reaction mixture was then brought to reflux for 2 hr. After cooling, the sodium chloride formed during the reaction was removed by filtration, and the resulting filtrate subjected to distillation. Most of the methanol was distilled and a fraction boiling between 66 and 105° (an azeotrope of methanol and α,α′-dimethoxydiethyl ether) was collected. To this fraction (about 100 ml) 10 g of freshly cut sodium was added and the mixture refluxed for 2 hr prior to distillation of the product through a 2-ft column packed with glass helices. α,α′-Dimethoxydiethyl ether was obtained (55 g, 65%) as a colorless liquid, bp 122–124° (*lit.*[16] bp 126–127°).

Anal. Calcd for $C_6H_{14}O_3$: C, 53.71; H, 10.52. Found: C, 53.69; H 10.45.

The β,β′-Dichlorodiethyl Acetal. To a 4-l. bottle, 780 g (9.7 mol) of 2-chloroethanol and 200 g of granulated anhydrous calcium chloride were added and cooled to 0°. Acetaldehyde (220 g, 5.0 mol) was slowly added to this mixture keeping the temperature below 10°, followed by the addition of 5 ml of concentrated hydrochloric acid. The bottle was well capped and the mixture allowed to stand for 2 days at room temperature with occasional shaking. The reaction mixture was filtered and washed with water and 5% sodium bicarbonate and then with water again before it was dried over magnesium sulfate. Fractional distillation of the anhydrous material yielded 650 g (74%), of the β,β′-dichlorodiethyl acetal, bp 78–79° (2.3 mm) (lit.[33] bp 106–107°, 14 mm).

The Divinyl Acetal.[34] In a 3-l., three-necked copper flask, 820 g (14.7 mol) of potassium hydroxide (from a freshly opened bottle) was heated and fused at 310° (estimated from the heating mantle). To the fused material, the β,β′-dichlorodiethyl acetal (300 g, 1.6 mol) was added over a period of 2 hr at about 280° with stirring (a stainless steel paddle and shaft must be used). After refluxing for 2 hr the mixture was subjected to distillation; the distillate was collected, washed with water, and dried over magnesium sulfate. Fractional distillation through a 2-ft column packed with glass helices yielded 51 g (26%) of the divinyl acetal: bp 101–103°; $n^{25}\mathrm{D}$ 1.4172 (lit.[34] bp 103°, $n^{20}\mathrm{D}$ 1.4200); nmr (neat) doublet centered at τ 8.58 (J = 5.0 cps, 3 H), doublet split into a quartet centered at 5.84 (J = 6.2 cps, J = −1.0 cps, 2 H), doublet split into a quartet centered at 5.53 (J = 13.6 cps, J = −1.0 cps, 2 H), quartet centered at 4.72 (J = 5.0 cps, 1H) and a doublet split into a quartet centered at 3.55 (J = 13.6 cps, J = 6.2 cps, 2 H).

The α,α′-Dichlorodiethyl Acetal. Anhydrous hydrogen chloride (22.6 g, 0.62 mol) was passed into the divinyl acetal (35 g, 0.31 mol), with stirring at −30 to −40°. It was found that above −10° the α,α′-dichlorodiethyl acetal decomposes to form acetaldehyde and α,α′-dichlorodiethyl ether[35] so that the reaction mixture was used immediately without further purification.

The α,α′-Dimethoxydiethyl Acetal. Freshly cut sodium (18.5 g, 0.8 mol) was completely dissolved in 500 ml of absolute methanol. After cooling to −30°, the α,α′-dichlorodiethyl acetal (77.6 g, 0.31 mol) was added using a hypodermic syringe. The mixture was kept under nitrogen at −30° with stirring for 1 hr. After refluxing for 1 more hr the mixture was cooled to room temperature and the salt that formed during the reaction was removed by filtration. Most of the methanol was then distilled from the filtrate. An azeotrope of methanol and the α,α′-dimethoxydiethyl acetal was then collected by distillation at reduced pressure. To this fraction (about 20 ml), 3 g of freshly cut sodium was added and the mixture refluxed for 2 hr, prior to fractional distillation through a 2-ft column packed with glass helices. This procedure yielded 12.5 g (68%) of the α,α′-dimethoxydiethyl acetal, bp 48.5–50° (2.0–2.5 mm). A minor fraction boiling at 110–113° (2 g) was shown to be α,α′-dimethoxydiethyl ether.

Anal. Calcd for $C_8H_{18}O_4$: C, 53.91; H, 10.18. Found: C, 53.87. H, 10.05.

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[31] S. O. Morgan and H. H. Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

[32] A similar reaction run at room temperature gave the same product at a lower yield (55%).

[33] J. A. Nieuwland, R. R. Vogt, and W. L. Foohey, *J. Amer. Chem. Soc.*, **52**, 1022 (1930).

[34] I. A. Arbuzova and K. Sultanov, *Vysokomol. Soedin.*, **2**, 1077 (1960); *Chem. Abstr.*, **55**, 8921*i* (1961).

[35] M. Goodman and G. C.-C. Niu, unpublished results.

Table VI[a]

Dipole Moment Analysis of Dimer Model Compounds

Sample	Isomer content		a_{exp} ($\pm$0.01)		b_{exp} ($\pm$0.02)	
	C_1 *meso*	C_2 racemic	*n*-Hexane	Benzene	*n*-Hexane	Benzene
1	0.5	99.5	1.71	2.22	+0.08	−0.25
2	3.4	96.6		2.31		−0.25
3	7.2	92.8	1.80		+0.09	
4	9.6	90.4		2.47		−0.26
5	11.7	88.3	1.86		+0.08	
6	14.2	85.8	1.92	2.58	+0.08	−0.25

[a] By solving four simultaneous equations, we obtain $a^{\mathrm{racemic}} = 1.70 \pm 0.08$ in *n*-hexane, 2.23 ± 0.07 in benzene; $a^{meso} = 3.19 \pm 0.08$ in *n*-hexane, 4.69 ± 0.07 in benzene.

Table VII

Dipole Moment Analysis of Trimer Model Compounds[a]

Sample	Isomer content			a_{exp} ($\pm$0.02)		b_{exp} ($\pm$0.02)	
	C_1 isotactic	C_2 syndiotactic	C_3 heterotactic	*n*-Hexane	Benzene	*n*-Hexane	Benzene
1	26.2	19.2	54.6	2.53	2.77	+0.01	−0.36
2	11.5	27.9	60.6	2.12	2.26	+0.01	−0.36
3	18.7	25.9	55.4	2.29	2.47	+0.01	−0.36
4	3.7	32.8	63.5		1.83		−0.36
5	5.2	22.5	72.3	2.07	1.99	+0.01	−0.36
6	0.0	55.7	44.3	1.46	1.48	+0.01	−0.36
7	2.2	37.1	60.7	1.81		+0.01	

[a] By solving six simultaneous equations, we obtain $a^{\mathrm{iso}} = 4.25 \pm 0.11$ in *n*-hexane, 4.83 ± 0.10 in benzene; $a^{\mathrm{syn}} = 0.78 \pm 0.11$ in *n*-hexane, 0.65 ± 0.10 in benzene; $a^{\mathrm{het}} = 2.33 \pm 0.11$ in *n*-hexane, 2.52 ± 0.10 in benzene.

Fractionation of α,α′-Dimethoxydiethyl Ether. The material obtained from the preparation as given consists of two isomers at a ratio of approximately 1:9 (*meso*-racemic). (Amounts of the two isomers were determined from peak areas in the nmr spectrum.) The optimum conditions found for fractionation were as follows: column temperature 70 ± 1°; injector temperature 170°; detector temperature 150°; helium flow rate 60 ml/min. When a 100-μl sample was injected, a smooth peak was obtained having a width of 23 ± 1 min. The vapor collected at Dry Ice-acetone temperature) was obtained in four fractions, 0–7, 7–13, 13–18, and 18–23 min, containing about 10, 20, 30, and 40%, rerespectively, of the total amount of material. This process was repeated until the first fraction totalled 0.8 ml; this fraction contained the isomers in a ratio of 14.2:85.8.

The fourth fraction (total 3.5 ml), which contained the isomers in a ratio of 7.2:92.8, was now refractionated, employing 100 μl of the sample for each injection. For this run, three fractions of the vapor were collected, 0–8, 8–15, and 15–23 min. *The fraction coming out between 15 and 23* min with isomer ratio 3.5:96.5 was then recycled through the column into three fractions with that portion coming off between 15 and 23 min being taken as the final sample (total amount 0.6 ml); the ratio of the two isomers in this sample was 0.5:99.5. The samples with intermediate composition were preserved for dipole moment measurements (Table VI).

Fractionation of the α,α′-Dimethoxydiethyl Acetal. The α,α′-dimethoxydiethyl acetal obtained by the above preparation consists of three isomers having a ratio of 1:2:4 (isotactic–syndiotactic–heterotactic) as determined from the nmr spectrum. The optimum conditions for fractionating this mixture were found to be as follows: column temperature 115 ± 1°; injector temperature 210°; detector temperature 185°; helium flow rate 60 ml/min. When a 250-μl sample was injected, under these conditions a smooth peak was obtained having a peak width of 53 ± 2 min. The vapor was collected (at −78°) in six fractions, 0–15, 15–25, 25–33, 33–40, 40–47, and 47–53 min, containing about 10, 10, 15, 20, 20, and 25%, respectively, of the total amount of material. This process was repeated until 0.8 ml was collected for the first fraction. Table VII lists the relative amounts of the isomers in these fractions.

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