An Experimental Study of the Conformational Energies of Poly(neopentyl Glycol Succinate)†

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Values of the dipole moment ratio $\langle\mu^2\rangle/nm^2$ of poly(neopentyl glycol succinate), obtained from dielectric measurements on dilute solutions of the polymer in benzene, varied from 0.548—0.586 in the temperature range 30—60 °C. From thermoelastic experiments, performed on polymer networks prepared by cross-linking hydroxy-terminated poly(neopentyl glycol succinate) chains, a value of 0.52×10^{-3} K^{-1} was obtained for the temperature coefficient of the unperturbed dimensions. Critical analysis of the thermoelastic and dielectric results, using the rotational isomeric state model, suggests that whereas the *gauche* states about the C–C bonds of the neopentyl glycol residue have an energy of *ca.* 0.6 kcal mol^{-1} lower than that of the alternative *trans* states, the former conformational states are disfavoured with respect to the corresponding *trans* states in the case of the central C–C bond of the succinyl residue. This study also suggests that the skeletal bonds of the type OC–C bonds are almost freely rotating.

From the critical interpretation of the dielectric properties of dialkyl esters of the type $(CH_2)_n(COOEt)_2$ having n = 0, 1, 2, 3, 4, and 8, Abe[1] obtained useful information for the study of the conformational properties of aliphatic polyesters. An important issue in these studies was to elucidate the preferred states about the CH_2CH_2–$COOCH_2$ bonds in polyesters. The available information is highly controversial.[1–5] From spectroscopic studies carried out on methyl propionate, some authors have concluded that the lowest-energy conformation arises when the C=O group eclipses the C–H bonds,[2] while other authors concluded that the C=O/C–C eclipsed form is more stable than the C=O/C–H eclipsed form.[3] The work performed by Abe[1] on dialkyl esters suggested that the dipole moment of most of the members of the series can be reproduced by assuming that the *gauche* states about the CH_2CH_2–$COOCH_2$ bonds are favoured over the alternative *trans* states by *ca.* 1.2 kcal mol^{-1}.‡ However, the theoretical calculations failed to reproduce the dipole moments of diethyl succinate.

Theoretical consideration that the C=O/C–C eclipsed form is strongly favoured over the alternative C=O/C–H form gives a high negative value for the temperature coefficient of the unperturbed mean-square end-to-end distance (d ln $\langle r^2\rangle_0/dT$) dimensions of poly(oxyneopentyleneoxyadipoyl) (PNA), in contrast with the experimental value which is positive.[6] In order to bring the theoretical value of this quantity close to the experimental result, it is required to assume that the CH_2-CH_2–$COOCH_2$ bonds are freely rotating. This is in agreement with the results of George *et al.*[5] which suggest that the C=O/C–H eclipsed form is only favoured by *ca.* 0.08 kcal mol^{-1} over the alternative C=O/C–H eclipsed form. A similar conclusion was obtained from the analysis of the configurational optical properties of some cycloaliphatic polyesters.[7]

Another important issue in the conformational analysis of polyesters is to elucidate the value of the energies associated with the rotational states about the central C–C bond of the succinyl residue. The information at hand is also controversial. N.m.r. spectroscopy studies performed by Zetta and Gatti[8] on liquid dimethyl succinate suggest that the *gauche* conformation is more stable than the *trans*. These results are at variance with the value derived for the conformational energies by using semi-empirical potential functions.[1]

This work forms part of a more general study on the conformational characteristics of aliphatic polyesters. The results obtained in this investigation may be used to predict the conformational properties of semiflexible polymers of the general formula $OCO(CH_2)_nCOOR$, where R possesses rod-like properties, which enable the polymer to form liquid crystals.

Experimental

Materials.—2,2-Dimethylpropane-1,3-diol (neopentyl glycol) was crystallized from a mixture of acetone–n-hexane (m.p. 131 °C; lit.,[9] 130 °C). Succinic acid was crystallized from distilled water at room temperature (m.p. 183 °C; lit.,[9] 182 °C) and toluene (Merck) was purified by conventional methods.[10]

Synthesis of the Polymer.—Poly(neopentyl glycol succinate) (PNS) was formed in toluene solution by reaction of equimolecular amounts of neopentyl glycol and succinic acid with toluene-*p*-sulphonic acid (1%) as catalyst. The reaction was carried out under reflux in a nitrogen atmosphere, and water formed in the condensation reaction was continuously separated by means of a Dean–Stark distillation trap. After 24 h a slight excess of neopentyl glycol was added and the reaction proceeded for a further 5 h. The polyester was precipitated with n-hexane and washed several times with water to eliminate the catalyst. In the final steps the polymer was dissolved in benzene, precipitated with n-hexane, and dried *in vacuo* for 24 h.

A fraction of number-average molecular weight 6 900, obtained by fractionating the product with chloroform–methanol, was used in the dielectric measurements and in the preparation of the networks utilized in the thermoelastic experiments. The melting temperature of the fraction, measured with a Perkin-Elmer DSC-4 calorimeter, at a heating rate of 8 K/min, was found to be 84 °C.

Dielectric Measurements.—Dielectric constants of solutions of PNS in benzene were measured using a capacitance bridge operating with a three-terminal cell.[11] The measurements were performed at 10 kHz; at this frequency the real part of the complex permittivity coincides with the static dielectric constant. The cell was calibrated with benzene, cyclohexane, and carbon

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† *Systematic nomenclature:* poly(oxy-2,2-dimethyltrimethyleneoxysuccinyl).

‡ 1 kcal = 4.184 kJ.

tetrachloride. The solvents were dried with molecular sieves immediately before use.

Differences between the refractive indices of the solutions (n) and the solvent (n_1) were measured at 638 nm with a Chromatix KHX differential refractometer.

Thermoelastic and Birefringence Experiments.—PNS networks were prepared by cross-linking hydroxy-terminated chains with equivalent amounts of 2,4-bis-(p-isocyanatobenzyl)phenyl isocyanate. The polymer and the cross-linking agent were dissolved in a small amount of chloroform (methanol-free). The solution was cast into a Teflon mould and the solvent was evaporated off. The cross-linking reaction was carried out at 80 °C for two days. The networks were extracted with chloroform and the soluble fraction was 0.15.

Thermoelastic and birefringence experiments were performed on unswollen strips using standard techniques. Elastic forces were measured with a pressure transducer (Gould Statham, model UC3); birefringence measurements were made by using a Babinet compensator in the manner described elsewhere.[12–14] Temperatures were in the range 60—110 °C, and in all the cases the strips were stretched at high temperature and held at this temperature until changes in the force and birefringence with time were not discernible. The measurements were made from high to low temperatures with some measurements out of sequence to test for reversibility.

Experimental Results

Values of the mean-square dipole moment $\langle\mu^2\rangle$ were determined as usual by means of the equation of Guggenheim and Smith.[15,16] The derivatives $d(\varepsilon - \varepsilon_1)/dw$ utilized in the equation were obtained from plots of the increments in the dielectric constant ε of the solution with respect to that of the solvent ε_1, against the weight fraction w of polymer. In the same way the values of $d(n^2 - n_1^2)/dw$ (n and n_1 being the refractive indices of solutions and solvent, respectively) were obtained from plots of $\Delta n = n - n_1$ against w. Results for $d(\varepsilon - \varepsilon_1)/dw$ and $d(n^2 - n_1^2)/dw$ at 30, 40, 50, and 60 °C are shown in the second and third columns of the Table, respectively. Values of the mean-square dipole moment are expressed in terms of the dipole moment ratio $\langle\mu^2\rangle/\text{nm}^2$ and are shown in the fourth column of the Table. The uncertainty of these values was estimated to be *ca.* 5%. In the evaluation[17] of nm², the mean-square dipole moment of the chain in the idealization that all the skeletal bonds are freely jointed, it was assumed that the dipole moment associated with each ester group of a repeating unit has a value[18] of 1.89 D. Moreover, the dipole moment corresponding to the C–C bonds and to the penultimate and ultimate C–O and O–H bonds have values of 0.00, 1.07, and 1.7 D, respectively.[19,20]

The temperature coefficient of the dipole moment of the PNS chains $d \ln \langle\mu^2\rangle/dT$ was obtained from the slope of the plot of the natural logarithm of the dipole moment ratio against temperature. The value of this quantity was 2.2×10^{-3} K⁻¹.

Preliminary results showed that unstrained PNS networks crystallize from the bulk at room temperature. Crystallization, however, was unattainable in samples kept at 60 °C for a long time. In order to investigate whether the orientation of the chains favours the crystallization of the networks, experiments were performed in the temperature range 60—110 °C in which the birefringence of the strained networks was measured as a function of the elongation ratio λ. For values of $1.4 < \lambda < 3$ and for a given temperature ($T > 60$ °C), the birefringence of the networks did not show a noticeable variation with time. Since the birefringence is very sensitive to crystallinity vestiges, these results suggest that crystallinity was not developed in the strained networks during the thermoelastic measurements.

Force-temperature results, represented in terms of $\ln(f^*/T)$ in Figure 1 for different elongation ratios, fit reasonably well to straight lines. The temperature coefficient of the unperturbed dimensions are obtained from the standard equation[21–24]

$$d \ln \langle r^2\rangle_0/dT = -[\partial \ln (f^*/T)/\partial T]_{p,L} - \beta/(\lambda^3 - 1)$$

where f^* is the elastic force referred to the undistorted cross-sectional area and β is the cubic expansion coefficient. The average value of $10^3\, d \ln \langle r^2\rangle_0/dT$, obtained from these plots was 0.52 ± 0.24 K⁻¹ and it closely approximates to the value of 0.46 reported for the temperature coefficient of the PNA chains.[6]

Table. Experimental dipole moments of poly(neopentyl glycol succinate)

T/°C	$d(\varepsilon - \varepsilon_1)/dw$	$d(n^2 - n_1^2)/dw$	$\langle\mu^2\rangle/\text{nm}^2$
30	2.229	0.036	0.548
40	2.177	0.025	0.562
50	2.111	0.016	0.572
60	2.059	0.004	0.586

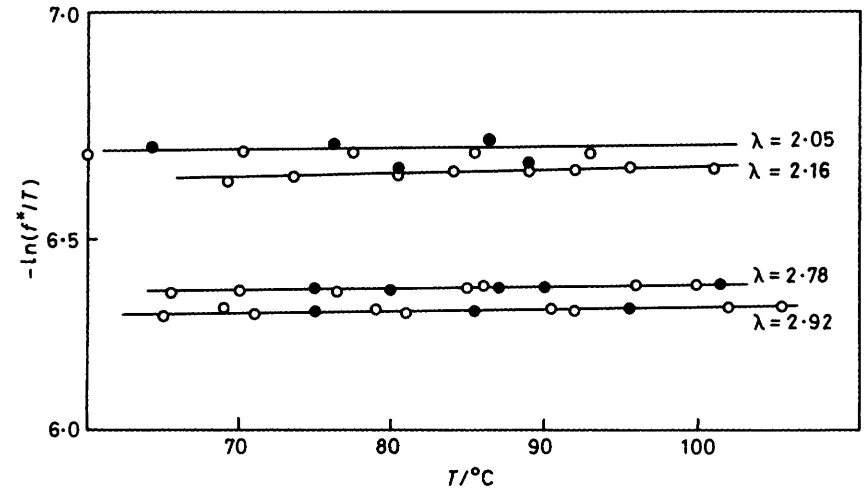

Figure 1. Force-temperature results for PNS networks at different elongation ratios λ. Open and filled circles represent the thermoelastic values $-\ln(f^*/T)$ obtained at decreasing and increasing temperatures, respectively

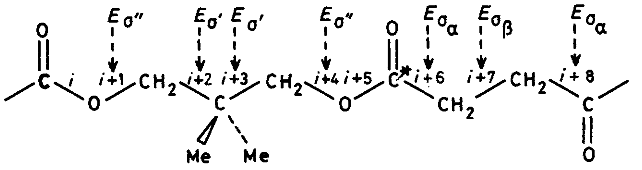

Figure 2. Repeating unit of PNS chains in the all-*trans* conformation

Conformational Energies

The repeating unit of PNS in an all-*trans* conformation is shown in Figure 2. Owing to the high rotational barriers of the ester C*–O bonds, i and $i + 5$ bonds are restricted to *trans* states. The potential curve associated with rotations about bonds of type $i + 1$ and $i + 4$ presents a well defined minimum centred at 0° (*trans* state) and two diffuse minima (*gauche* states) located at ±75 °C, the energy of which is *ca.* 1.2 kcal mol^{-1} above that of the alternative *trans* states.[6] For rotational angles lying in the range 80—280°, strong interactions between the methyl and the carbonyl groups occur which cause the rotational energy to increase to several hundreds of kcal mol^{-1}.

Gauche rotations about the C–C bonds of the neopentyl glycol residue give rise to first-order interactions between an oxygen atom and a methyl group. Although potential calculations suggest that the *gauche* states should be slightly preferred over the corresponding *trans* states, the critical analysis of the dipole moment of poly-(3,3-dimethyloxetane) (PDO)[25,26] and PNA[6] indicates that *gauche* states have a conformational energy $E_{\sigma'}$ of 0.6—0.7 kcal mol^{-1} less than that of the alternative *trans* states.

As indicated above, there is great discrepancy[1–6] among the values reported for the conformational energies associated with the rotational states of the skeletal bonds of type $i + 6$ and $i + 8$. Critical interpretation of the temperature coefficient of the unperturbed dimensions of PNA suggests that the energy E_{σ_α} associated with *gauche* states has almost the same value as that of the alternative *trans* states.[6] Obviously these results are in sharp disagreement with those reported by Moravie and Corset[3] according to which the C=O/C–C eclipsed form is more stable than the C=O/C–H eclipsed form.

Gauche rotations about the central C–C bond of the succinyl residue give rise to first-order interactions between two consecutive carbonyl groups. Non-bonded interactions between atoms separated by more than two bonds were computed by a 6–12 Lennard–Jones potential using the parameters summarized in references 6 and 27—29. A barrier of V_0 = 2.8 kcal mol^{-1} was used for the torsional potential[27,28] about the C–C bond. Dipole–dipole energies were calculated by assigning partial charges to the ester group ($q_C^* = -q_O^* = 0.318$ and $q_C = -q_O = 0.006$) which reproduce the dipole moment of 1.89 D of the ester group.[30] As usual, a value of $\varepsilon = 3$ was utilized for the effective dielectric constant. The potential curve indicates that *gauche* states have an energy E_{σ_β} of *ca.* 0.6 kcal mol^{-1} above that of the corresponding *trans* states. The result is in fair agreement with the value of 0.35 kcal mol^{-1} obtained by Abe[1] for this conformation using Buckingham potential functions for the evaluation of non-bonded interactions. It should be pointed out that recent calculations[31] carried out using STO-3G and MNDO give conflicting results for E_{σ_β}. Thus, whereas slight preference for *gauche* states is obtained in the former method, preference is for the *trans* states in the latter.

As indicated elsewhere,[6] *gauche* rotations of different sign about two consecutive C–C bonds of the glycol residue were assumed to have an energy E_ω of 0.6 kcal mol^{-1}. Rotations of different sign about any other pair of consecutive bonds were considered to be forbidden with the exception of $i + 1$, $i + 2$ and $i + 3$, $i + 4$ pairs of bonds where the conformations have energies of $E_{\sigma'} + E_{\sigma''}$, and $E_{\sigma''}$, respectively.

Theoretical Results

Values of the dipole moment ratio and the temperature coefficient of both the dipole moment ratio and the unperturbed mean-square end-to-end distance were calculated for hydroxy-terminated chains using statistical mechanics methods described in detail elsewhere.[17,32] It was assumed that the magnitude of the dipole moment associated with each ester group is 1.89 D and its direction makes an angle of 123° with the direction of the R–C* bond.[18] The dipole moments corresponding to the ultimate H–O and penultimate C–O bonds lie along the respective skeletal bonds. All the rotational angles were considered to be located at 0 ± 120°, with the exception of the C–O bonds whose *gauche* states are at ±75° and the C*–O bonds which are restricted to *trans* states. Bond lengths and bond angles used in the calculations are given in references 6 and 33.

The dependence of the dipole moment and its temperature coefficient on the conformational energies discussed above were studied utilizing the main set of energies: $E_{\sigma'} = -0.6$, $E_{\sigma''} = 1.2$, $E_{\sigma_\alpha} = 0.00$, $E_{\sigma_\beta} = 0.6$, and $E_\omega = 0.6$ kcal mol^{-1}. The sensitivity of $\langle\mu^2\rangle/\text{nm}^2$ and d ln $\langle\mu^2\rangle/\text{d}T$ to the *gauche* population about the C–C bonds of the glycol residue was investigated for two values of E_{σ_α} (0.00 and 1.2 kcal mol^{-1}). The results obtained are shown in Figure 3. As expected upon increasing the value of $E_{\sigma'}$ the dipole moment ratio also increases as a consequence of the fact that the fraction of *trans* conformation for which the dipole vectors of two consecutive ester groups are in almost parallel directions rises. For the same reason, the temperature coefficient of the dipole moment increases as $E_{\sigma'}$ decreases. For $E_{\sigma_\alpha} = 0.0$ kcal mol^{-1}, very good agreement between the experimental values of $\langle\mu^2\rangle/\text{nm}^2$ and d ln $\langle\mu^2\rangle/\text{d}T$ and the corresponding theoretical ones is obtained for $E_{\sigma'} = -0.6$ kcal mol^{-1}, the value obtained for this quantity in a previous analysis of the configurational properties of PNA.[6] The curves that show the dependence of the dipole moment ratio and its temperature coefficient on $E_{\sigma'}$ for $E_{\sigma_\alpha} = 1.2$ kcal mol^{-1} are located, respectively, below and above from those obtained assuming that bonds of type $i + 6$ and $i + 8$ are freely rotating. In general, the variation of the dielectric configurational properties with $E_{\sigma'}$ are less pronounced in the former case than in the latter. For $E_{\sigma_\alpha} = 1.2$ kcal mol^{-1}, to bring the theoretical value close to the experimental dipole moment ratio would require that $E_{\sigma'} = -0.4$ kcal mol^{-1}; however, agreement between theoretical and experimental values in the case of the temperature coefficient of the dipole moment would be obtained using for $E_{\sigma'}$ the unlikely value of 0.2 kcal mol^{-1}.

Conformational analysis (n.m.r. spectroscopy) of aqueous succinic acid and liquid dimethyl succinate[31] indicate that the *gauche* states are preferred over the alternative *trans* states. However, conflicting results are obtained for the values of the conformation energies in the gaseous state, or in presence of solvents where the solute–solvent interaction will not alter the relative population of rotational states.

An examination of the repeating unit of PNS suggests, at first glance, that the polarity of the chains should be very sensitive to the relative fraction of rotational states about the central C–C ($i + 7$) bond. If the skeletal bonds of the succinyl residue are kept in an all-*trans* conformation, the dipoles associated with the consecutive ester groups flanking the succinyl residue have almost opposite directions. Therefore removal of the *trans* conformations will increase the polarity of the chains. The variation of $\langle\mu^2\rangle/\text{nm}^2$ with conformational energies E_{σ_β} and

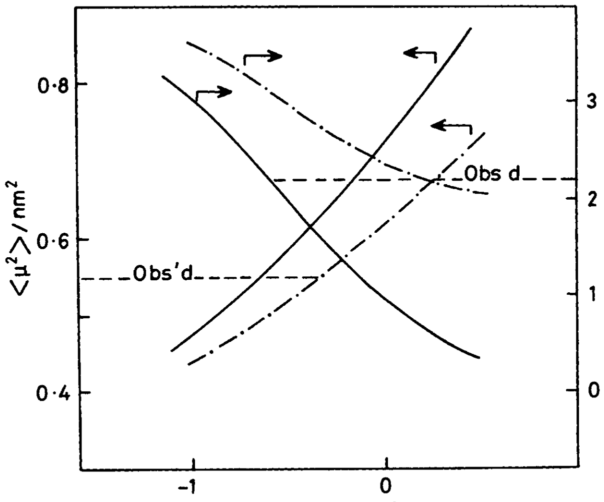

Figure 3. Dependence of the dipole moment ratio and its temperature coefficient on $E_{\sigma'}$ for $E_{\sigma_\alpha} = 0.0$ (——) and $E_{\sigma_\alpha} = 1.2$ kcal mol^{-1} (–·–·)

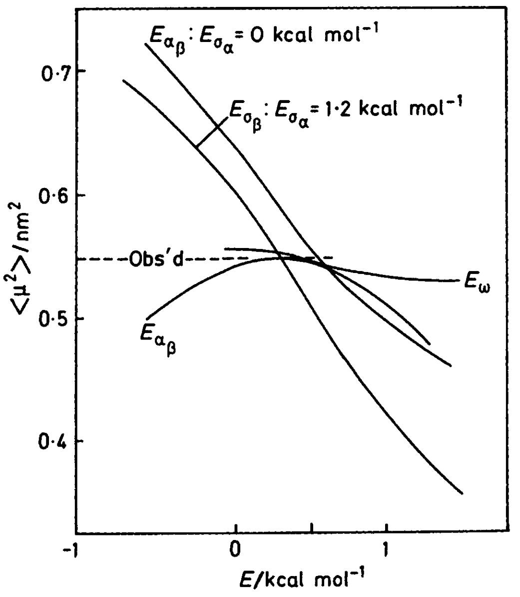

Figure 4. Values of the dipole moment ratio as a function of the conformational energies E_{σ_α}, E_{σ_β}, and E_ω

E_{σ_α} is shown in Figure 4. It can be seen that the more important change in the polarity of the chains occurs with E_{σ_β}. Thus in decreasing E_{σ_β} from 1.4 to −0.56 kcal mol^{-1}, the dipole moment ratio increases from 0.48—0.72 for $E_{\sigma_\alpha} = 0$ kcal mol^{-1}. These changes are larger if the value of E_{σ_α} is considered to be 1.2 kcal mol^{-1}; in both cases agreement between theoretical and experimental results is obtained for $E_{\sigma_\beta} \approx 0.5$ and 0.3 kcal mol^{-1}, respectively. Therefore these results seem to suggest that *gauche* states about the C–C bonds of the succinyl residue which cause first-order interactions between two carbonyl groups are disfavoured with respect to the *trans* states. Similar conclusions can be drawn from the theoretical analysis of the dipole moment of ethyl succinate;[1] in order to obtain a good fit of the experimental results using $E_{\sigma_\alpha} = 1.2$ kcal mol^{-1}, it would be required that the energy of the *gauche* states about the C–C bonds be *ca.* 1 kcal mol^{-1} below that of the alternative *trans* states. The plots of Figure 4 also indicate that the changes of $\langle\mu^2\rangle/\mathrm{nm}^2$ with E_{σ_α} and E_ω are less pronounced than with E_{σ_β}.

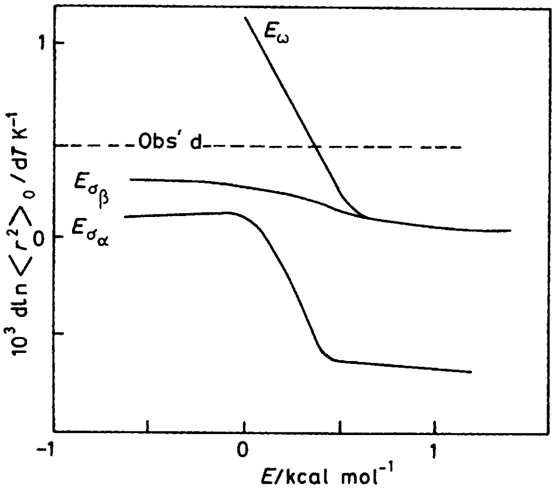

Figure 5. Theoretical values of the temperature coefficient of the unperturbed dimensions as a function of the conformational energies E_{σ_α}, E_{σ_β}, and E_ω

As previously discussed in the Experimental section, the analysis of the thermoelastic results suggests that the unperturbed dimensions have a moderate and positive temperature dependence. For $E_{\sigma_\alpha} = 1.2$ kcal mol^{-1}, the values of d ln $\langle r^2\rangle_0$/dT are negative for values of $E_{\sigma'}$ lying in the range -1—0.5 kcal mol^{-1}. Positive values of d ln $\langle r^2\rangle_0$/dT are only obtained for $E_{\sigma_\alpha} \approx 0$ and $E_{\sigma'} < -0.5$ kcal mol^{-1}, suggesting that the C*–C bonds are freely rotating. These results in conjunction with those obtained for PNA chains[6] argue against the assumption that *gauche* states about these bonds are strongly disfavoured with respect to the *trans* states.[3]

The variations of d ln $\langle r^2\rangle_0$/dT with conformational energies E_{σ_α}, E_{σ_β}, and E_ω are shown in Figure 5. The results indicate that whereas the unperturbed dimensions are extremely sensitive to E_{σ_α} and E_ω, they are almost insensitive to the relative population of rotational states about bonds of type $i + 7$. The curve representing the dependence of d ln $\langle r^2\rangle_0$/dT on E_{σ_α} shows that the value of the temperature coefficient is negative and almost constant for $E_{\sigma_\alpha} \geqslant 0.4$ kcal mol^{-1}, but its sign becomes positive for $E_{\sigma_\alpha} \approx 0$ kcal mol^{-1}. In any case, using the main set of conformational energies given above, the value of d-ln $\langle r^2\rangle_0$/dT lies below the experimental result even if values of $E_{\sigma_\alpha} < 0$ are used. The data of Figure 5 suggest that in order to bring the theoretical values close to the experimental results, it would be required that the conformational energy E_ω associated with *gauche* rotations of different sign about two consecutive C–C bonds of the glycol residue have the reasonable value of *ca.* 0.4 kcal mol^{-1}.

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