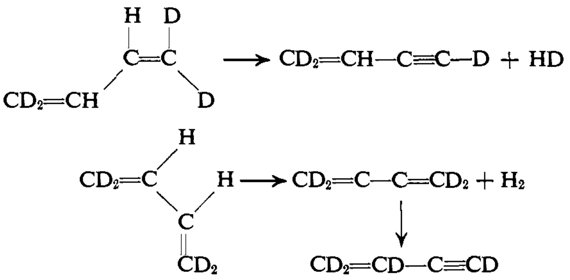
(2a)

(2b)

stable molecule. The diminution in the yield of vinylacetylene on the addition of oxygen is puzzling. Perhaps radicals such as the one formed in the first step of (2b) can react with oxygen.

The reactions described here are somewhat similar to the thermal rearrangements observed in 7-deuterio-1,3,5-cycloheptatriene.[12] Since the photochemical reactions of butadiene in the vapor phase have been shown[4] to take place from the vibrationally excited ground state that is formed by internal conversion from the initially produced singlet excited state, the rearrangements observed in the present instance are also thermal processes. The principal difference between the two systems is that in 1,3,5-cycloheptatriene there is no chemical change which accompanies the migration of deuterium (or hydrogen), whereas in butadiene there is always a chemical change. In butadiene one migration of hydrogen has to be followed by a second migration if the molecule is to be regenerated. This pathway may be prohibited to a highly excited (*ca.* 100 kcal/mole) molecule such as the one that is produced by internal conversion from the upper singlet state. The extension of these results to other conjugated diene and triene molecules should be of considerable interest.

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The Vapor Phase Photolysis of Benzene at 1849 A

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Contribution from the Department of Chemistry, University of California, Riverside, California. *Received January 3, 1966*

Abstract: The quantum yield of disappearance of benzene vapor at 1849 A is 0.9 ± 0.3. The major irradiation product appears to be a valence isomer of benzene, tentatively identified as "benzvalene." Addition of diluent N_2 reduces the rate of formation of the product but, up to 50 mm total pressure, increases its maximum concentration. Small amounts of fragmentation products, *i.e.*, methane, ethane, ethylene, and acetylene, are also observed, as well as considerable amounts of polymeric or carbonaceous deposit on the cell walls. These products may be formed in the secondary photolysis of "benzvalene."

The photochemistry of benzene has been studied in the gas phase,[2-4] the liquid phase,[5-8] and the solid phase;[3] however, little is known of the products or mechanism of its decomposition. In the solid phase, Gibson suggested that 1,3,5-hexatriene was a product,[8] while Bryce-Smith reported the formation of fulvene in the liquid phase. In the gas phase Noyes[2a] reported that below 2000 A the only volatile products formed were hydrogen, acetylene, and methane. He also concluded that the only major nonvolatile product, the solid material always found on the windows of a benzene photolysis cell, was most probably an acetylene polymer similar to cuprene. Shindo and Lipsky[4] have recently observed the ultraviolet spectrum of a product of the 1849-A photolysis of benzene vapor which was similar in appearance to that of biphenyl vapor.

Recent work on the spectroscopy and energy-transfer processes of electronically excited benzene[9-12] and its simple homologs has shown that the energy absorbed by benzene in its first absorption band (2300–2700 A) is efficiently dissipated by photophysical processes (*i.e.*, internal conversion and/or emission), while that absorbed in its second and third bands (λ_{max} at 2200 and 1800 A), cannot be accounted for by such processes. For reference, a benzene spectrum complete with band assignments is shown in Figure 1. As the photochemical data for benzene are inadequate and even somewhat ambiguous in the lower wavelength regions, and in view of the implications of the recent spectroscopic data, we felt it desirable to attempt a new study utilizing the newer analytical methods which have become available since Noyes' early work.

Experimental Section

Two reaction cells and concomitant irradiation systems were used. Cell 1 was a 50-mm Pyrex tube, blown closed at one end, with a

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(1) Author to whom communications should be addressed.

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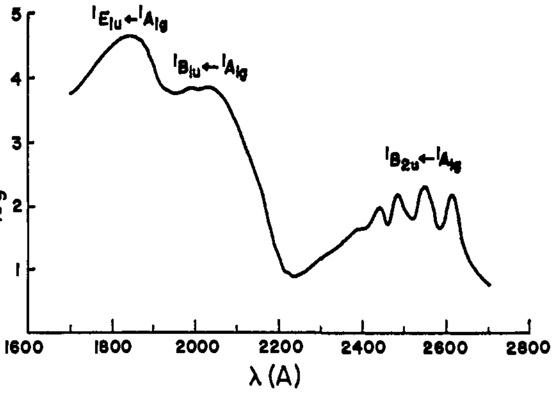

Figure 1. Liquid phase ultraviolet absorption spectrum of benzene including symmetry assignments of the three bands. Extinction coefficients are in units of mole $l.^{-1}$ cm^{-1}.

Suprasil window attached by Glyptal at the other end. Its volume was 279 ml. At the opposite end from the window, a 2-mm capillary tube led to a "T" from which samples could either be removed to a gas chromatograph by means of a Pratt-Purnell valve[13] or the cell could be evacuated or filled from a conventional vacuum line which was carefully kept free of mercury to avoid mercury-sensitized reactions at 2537 or 1849 A. The cell was irradiated at 1849 A with the uncollimated beam from a flat, helix-wound Hanovia SC 2537 lamp which had the same diameter as the cell. The gas space between the lamp and the cell (*ca.* 5 mm) was flushed with N_2 to reduce absorption of the 1849-A light by atmospheric O_2. No attempt was made to remove 2537-A light as no reaction leading to noncondensables ($\Phi < 0.001$) or condensables ($\Phi < 0.01$) was observed on irradiation at 2537 A. No shutter was used; therefore zero time for a run was taken as the time of introduction of the sample into the cell. The cell temperature was controlled by use of a heating tape wound around the reaction zone of the cell. Temperature was measured by a thermocouple in a thermal well 2 mm from the cell window.

Cell 2 was a Pyrex "T" cell of *ca.* 300-ml volume which was filled on a mercury-free vacuum line and then placed in the Cary 15 sample compartment, modified as shown in Figure 2. Benzene pressure was kept in the region of $55-66 \times 10^{-3}$ torr for all runs in cell 2 by filling from a benzene reservoir held at −64° by a chloroform-slush bath. Actual pressures were obtained by determining the absorbance of the cell contents in the Cary 15 at 2000 A and using the extinction coefficient $\epsilon_{2000A} = 0.360$ cm^{-1} $torr^{-1}$.[14] The cell windows transmitting the Cary 15 light beam were of optical quartz; the third window through which the sample was irradiated was of Suprasil. The same helical Hg lamp was used as that employed for the runs with cell 1. The light beam was passed through a 4-in. long, 2-in. diameter piece of blackened "Hexacell" aluminum aircraft structural material between the lamp and the cell. The honeycomb structure of this material conveniently provided an approximately collimated beam of light. The air space between the lamp and cell was again purged with N_2 to reduce O_2 absorption of 1849-A radiation.

Chemicals. Benzene was Matheson Chromatograde, purified further by preparative chromatography and stored under vacuum. Nitrogen was prepurified grade, purified for some runs over Cu held at 450° to remove the last traces of O_2. N_2O was Matheson CP grade used without further purification.

Actinometry. Actinometry was only attempted with cell 1. The photolysis of N_2O, shown in the literature to give $\Phi_{N_2} = 1.4$ at room temperature,[15-17] was followed by gas chromatography using a 13X molecular sieve column and a thermal conductivity detector, both at room temperature. The pressure of N_2O at the start of each run was adjusted so that the effective cell length (*i.e.*, to 99% absorption of 1849-A light) was the same as in the corresponding benzene runs. Because of the deposition of the opaque polymeric product on the cell window during each run, the actinometer runs were alternated with the benzene runs, and only initial rates of appearance of products and disappearance of benzene were accepted as meaningful.

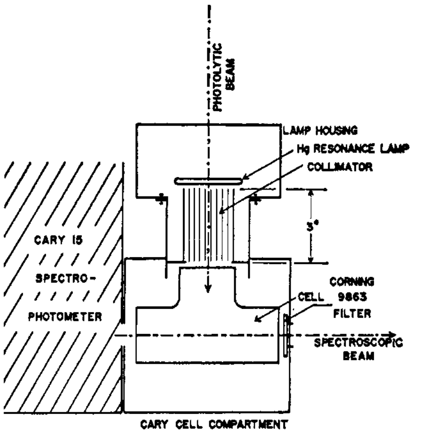

Figure 2. Alignment of cell 2 for photolyses carried out in the Cary 15 sample compartment.

Product Analysis. Products from cell 1 were analyzed by gas-liquid chromatography using H_2 flame detection. For low-boiling products, *i.e.*, CH_4, C_2H_2, etc., a 20-ft long column of 20% Squalane on 60/80 Chromosorb W was used at 50°. Benzene concentration was followed using a 15-ft long 5% SE 30 on 60/80 firebrick column at 100°.

Results

The runs shown in Table I were made using cell 1. The benzene concentration was followed as a function of time, and the initial rate of disappearance of benzene was then obtained by establishing the slope of the benzene concentration *vs.* time plot at zero time. These, in turn, were compared to N_2O actinometer runs, carried out prior to each irradiation, to establish the quantum yield of disappearance of benzene. Runs were 40–100 min in total length depending upon the light intensity available for the run. The conversion of benzene at the first points obtained on these runs was approximately 5%. The initial slope determination was imprecise because of the relatively long period (*ca.* 12 min) between samples required by the chromatographic analysis system. Thus the estimates of error in Table I are relatively high estimates of *absolute* error.

The quantum yields of appearance of acetylene were obtained in a similar manner. In this case the determination of the original slope was more precise, as samples could be removed at smaller time intervals, leading to lower estimates of error. The data are shown in Table II.

A major, as yet unidentified, irradiation product was observed to form at a high initial rate reaching a relatively low maximum concentration. By comparing retention times of this product on both Ucon-polar and Squalane columns, we suggested that the product is a highly unsaturated C_6 hydrocarbon, perhaps a valence isomer of benzene.[3] This product will be referred to here as i-C_6H_6. Its retention time on Ucon-polar does not correspond to that given in the literature for "Dewar" benzene; the relative retention time of "Dewar" benzene *vs.* benzene is 0.47 while that of i-C_6H_6 is 0.93. Similar data are unavailable for other benzene isomers.

Qualitative photolyses in cell 1, using an Hanovia SH lamp with a water filter passing radiation longer

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Table I. Quantum Yields of Benzene Disappearance at 1849 A

Run	Temp, °C	$(I_a)_0$, quanta sec^{-1}	$\Phi_{C_6H_6}$	$(P_{C_6H_6})_0$, torr × 10^3	Total pressure, torr
1	85 ± 5	6.6×10^{14}	-1.1 ± 0.3	86	8.6
2	35 ± 5	3.0×10^{15}	-1.0 ± 0.3	82	8.2
3	35 ± 5	1.8×10^{15}	-0.8 ± 0.3	94	9.4

Table II. Quantum Yields of Acetylene from Benzene Irradiation at 1849 A

Run	Temp, °C	$(P_{C_6H_6})_0$, torr × 10^3	Total pressure, torr	$(I_a)_0$, quanta sec^{-1}	$(\Phi_{C_2H_2})_0$
4	35 ± 5	78	7.8	5.7×10^{15}	0.010 ± 0.005
5	35 ± 5	75	7.5	4.7×10^{15}	0.015 ± 0.005

than 1920 A, also showed decomposition of benzene. However, when a saturated NaCl solution was substituted for the water filter, the rate of disappearance of benzene was reduced by about 100-fold. Comparison of the emission of these two lamp-filter systems showed that the light responsible for the reaction was a band from 1920 to 2200 A, with a maximum at about 2100 A.

Photolyses in "T" cell 2 were monitored continuously with the sample beam of the Cary 15 spectrophotometer. An absorption peak at 2420 A was found to increase during a photolysis; this was followed as a function of time. Initial benzene pressures for all runs in this cell were 55–66 × 10^{-3} torr, and diluent N_2 was added to various total pressures. The plots of absorbance at 2420 A. *vs.* time for these runs are shown in Figure 3.

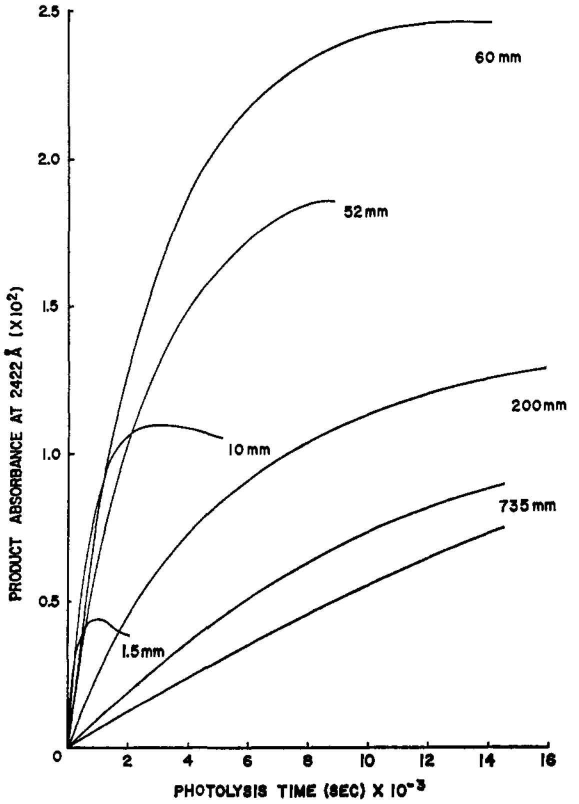


Figure 3. Increase of product absorbance with time. The pressure of diluent nitrogen is shown with each curve.

The ultraviolet spectrum of the product is shown in Figure 4. Maximum conversion in these runs was approximately 30%. In the dark, the absorbance of the product dropped very slowly, indicating that at these low pressures it was relatively stable at room temperature.

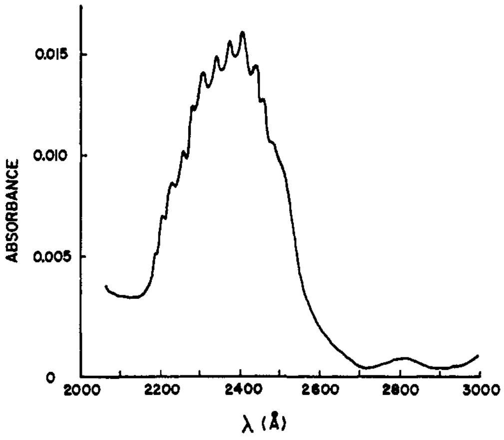


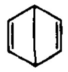
Figure 4. Ultraviolet spectrum of i-C_6H_6.

The absorbed light intensity decreased by a factor of one-third during this series of runs as estimated by comparing two identical runs at the start and end of the series and assuming that rate of appearance of i-C_6H_6 was proportional to light intensity. By further assuming that this reduction was linear with irradiation time, the rates of products appearance for all runs were normalized to a single light intensity in order to facilitate their comparison.

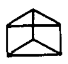
Discussion

In accord with Wilson and Noyes,[2a] we find that the major ultimate product of the 1849-A vapor phase photolysis of benzene is a carbonaceous or polymeric deposit on the walls and windows of the reaction vessel. We also confirm their low quantum yields of the dissociative products methane and acetylene as well as observing traces of ethane, ethylene, and what appeared to be toluene. Hydrogen, reported as a product by Wilson and Noyes, was not determined since a hydrogen flame detector was used in our analysis. While these fragmentation processes are minor at 1849 A and, within experimental error, absent at 2537 A, the quantum yield of disappearance of benzene at 1849 A is about 0.9 ± 3. As noted earlier, this is consistent with the spectroscopic data of Braun, Kato, and Lipsky.

Although we have no specific information as to the extinction coefficient of i-C_6H_6 at 2420 A, it would appear that it represents a major portion of the disappearing benzene. In considering its possible structure, we note that recent studies of the photoisomerizations of polyalkylbenzenes[19-24] have proved that alkyl group migrations are accompanied by ring carbon migrations. The mechanisms proposed involve valence isomers of the substituted benzenes, particularly the "Dewar" benzene (I), "benzvalene" (II), and "prizmane" (III) structures. Direct comparison of these studies with our work on benzene is complicated by the differences in wavelengths and monochromatic character of the light employed. In all of the polyalkylbenzene isomerizations cited, light above 2000-A wavelength was used, while we have used the Hg resonance radiation at 1849 A. This difference may not be as important as one might expect. Thus, as seen in Figure 1, 1849-A radiation is absorbed in the $^1E_{1u}$ band of benzene. Since the electronic spectra of the polyalkylbenzenes, particularly the poly-t-butylbenzenes, are similar to benzene but shifted toward the red from benzene by as much as 200 A, the electronic states with which we are dealing in this study may be similar to those involved in the alkylbenzene isomerizations, where the wavelengths of light were slightly longer than ours. Recognizing the possible pitfalls of the comparison, it is not unreasonable to suggest that in our vapor phase system it has been possible to form and stabilize a molecule of structure similar to the intermediate responsible for the isomerization of the alkylbenzenes.


I


II


III

Of the possible structures, one can eliminate "Dewar" benzene based on chromatographic evidence and based on its lack of an ultraviolet absorption maximum in the 2400-A region.[18] "Prizmane" can also be eliminated based on an extrapolation of the known ultraviolet absorption of 1,2,3-tri-t-butyl-4,5,6-trifluoroprizmane.[25] 1,3,4-Trifluoro-2,5,6-tri-t-butyltricyclo[2.1.1.0^{5,6}]hex-2-ene[25] (*i.e.*, a substituted benzvalene) does, however, have an ultraviolet absorption maximum at 2320 A (ϵ 2500 l. mole^{-1} cm^{-1}), suggesting that its unsubstituted parent might absorb at 2400 A. One further benzene isomer, fulvene (IV), also has an absorption maximum at about 2400 A (ϵ 14,000 l. mole^{-1} cm^{-1})[26] and must be considered as a possible product, particularly in view of the observations of Bryce-Smith and co-workers in the solution phase.[5,6] If indeed our intermediate has the same structure as that responsible for the alkylbenzene isomerizations, the most probable of the two possible compounds is benzvalene, as it would be expected to isomerize easily to benzene[25] while fulvene would not.

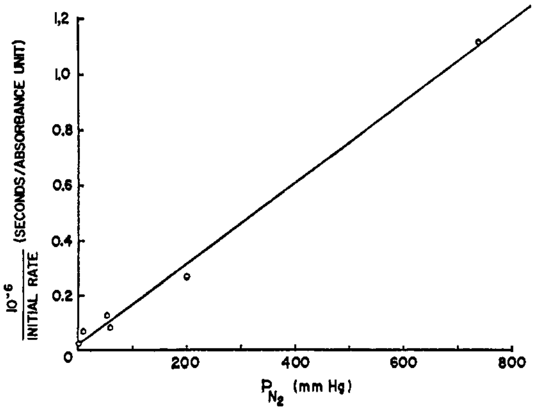


Figure 5. Relative initial rates of formation of i-C_6H_6 as a function of nitrogen pressure.

While lack of specific identification of the i-C_6H_6 formed in this system is a hindrance to establishment of a specific reaction mechanism, on the basis of the measured relative initial rates of its formation and the effects of pressure on these rates (Figure 2), one can propose the following mechanism at 1849 A

$$C_6H_6 + h\nu \longrightarrow C_6H_6(^1E_{1u}) \quad \text{(I)}$$

$$C_6H_6(^1E_{1u}) \longrightarrow i\text{-}C_6H_6^* \quad (1)$$

$$M + C_6H_6(^1E_{1u}) \longrightarrow C_6H_6 \text{ or products other than } i\text{-}C_6H_6 \quad (2)$$

$$M + i\text{-}C_6H_6^* \longrightarrow i\text{-}C_6H_6 \quad (3)$$

$$i\text{-}C_6H_6^* \longrightarrow \text{products other than } i\text{-}C_6H_6 \text{ or benzene} \quad (4)$$

where the asterisks represent either electronically or vibrationally excited molecules.

Recent evidence[9,27,28] suggests that no photophysical processes are responsible for energy dissipation when benzene is excited with light below approximately 2400 A. Therefore spectroscopic photophysical processes of benzene in the $^1E_{1u}$ state are neglected. Assuming the steady-state approximation for $(i\text{-}C_6H_6)^*$ and the $C_6H_6(^1E_{1u})$, we obtain

$$\frac{I_a}{(R_{i\text{-}C_6H_6})_0} = 1 + \frac{k_2k_4}{k_1k_3} + \frac{k_2[M]}{k_1} + \frac{k_4}{k_3[M]}$$

where $(R_{i\text{-}C_6H_6})_0$ is the initial rate of formation of the intermediate. As $(R_{i\text{-}C_6H_6})_0 = K(\mathrm{d}A_{2420})_0/\mathrm{d}t = K(R_A)_0$

$$\frac{I_a}{K}\left(\frac{1}{R_A}\right)_0 = 1 + \frac{k_2k_4}{k_1k_3} + \frac{k_2[M]}{k_1} + \frac{k_4}{k_3[M]}$$

The I_a normalized values of $(1/R_A)_0$ are plotted *vs.* P_{N_2} in Figure 5. The straight-line dependence of $(1/R_A)_0$ with P_{N_2} indicates that $k_2[M]/k_1 >> k_4/k_3[M]$ within the pressure range studied. In other words, the collisional quenching of the excited benzene molecule is very rapid in comparison to its conversion to an excited i-C_6H_6, and, that once this conversion has

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taken place, the collisional relaxation of $i\text{-}C_6H_6$ is much faster than further reaction of $i\text{-}C_6H_6$. This perhaps explains why this $i\text{-}C_6H_6$ is not observed in condensed phases. At high pressures, as in solution, its rate of production would be vanishingly low. Finally, the eventual drop in concentration of $i\text{-}C_6H_6$, as shown in Figure 2, can be attributed to its secondary photolysis or sensitized decomposition by excited benzene. This in conjunction with its low rate of production would, of course, reduce its steady-state concentration in condensed phases to unobservable levels.

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Dipole Moments of Chain Molecules. I. Oligomers and Polymers of Oxyethylene

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Contribution from the Departments of Chemistry, The Polytechnic Institute of Brooklyn, Brooklyn 1, New York, and Stanford University, Stanford, California.

Received April 12, 1966

Abstract: Mean-square dipole moments have been calculated for oxyethylene chain molecules $RO(CH_2CH_2O)_xR$, where $R = H$ or C_2H_5 and $x = 1\text{–}120$, using a rotational isomeric state model with neighbor dependence. In a previous study of polyoxyethylene, the mean extension of the chain and its temperature coefficient were used to obtain statistical weights for rotational states about skeletal bonds. These statistical weights, with minor modification, are shown to give dipole moments in good agreement with measured values over a wide range of molecular weight. A comparatively large, positive temperature coefficient of the dipole moment is predicted for polyoxyethylene.

The rotational isomeric state model has been notably successful in the interpretation of the random coil configurations of an impressive list of long-chain molecules: polyisobutylene,[1] polyethylene,[2,3] poly(dimethylsiloxane),[4] polyoxymethylene,[5] polyoxyethylene,[6] polypeptides,[7] and vinyl polymers of both regular and irregular steric structure.[8] In these cases, the efficacy of the model was put to test by comparison of calculated and measured values of (i) the *characteristic ratio* $\langle r^2\rangle_0/nl^2$ of the mean-square end-to-end distance of the chain unperturbed by long-range interactions to the same mean-square dimension nl^2 in the idealization that all skeletal bonds of the chain are freely jointed, and usually also of (ii) the temperature coefficient $d \ln \langle r^2\rangle_0/dT$ of these unperturbed dimensions. Experimental methods permit the determination of these two quantities only for high molecular weight materials. Recent advances in theory[9] permit calculation of the mean-square moment which is the resultant sum of any set of vector quantities associated with the respective skeletal bonds of a chain molecule, irrespective of its degree of polymerization. The mean-square dipole moment of a chain molecule consisting of units having dipole moments is such a quantity. It can be measured with considerable accuracy over a wide range of molecular weight. This experimental quantity is therefore ideally suited for a test of theory in the interesting region of short chain length, where the properties of a chain molecule change most rapidly with molecular weight. An important step in this direction is the successful interpretation[10] of the dipole moments of α,ω-dibromo-*n*-alkanes in the low molecular weight region, using statistical weights calculated from spectroscopic investigations on *n*-alkanes and *n*-alkyl bromides and supported by the statistical analysis of the polyethylene chain.[2,3]

This paper is concerned with mean-square dipole moments of chain molecules having dipolar skeletal bonds. Specifically, dipole moments of oligomers and polymers of oxyethylene are calculated using statistical weights appropriate for the interpretation of $\langle r^2\rangle_0/nl^2$ and $d \ln \langle r^2\rangle_0/dT$ of polyoxyethylene. The interdependence of bond rotational states, manifested in the repression of conformations in which neighboring bonds adopt *gauche* rotational states of opposite sign, is taken into account as described previously.[6] Calculations are compared with experimental results reported in the literature.

Theory

Rotational Statistical Weights. The polyoxyethylene chain is shown in its planar *trans* conformation in Figure 1. The end groups R for the two series of homologs to be considered are C_2H_5 and H. The

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