Dipole Moments of Chain Molecules. II. Poly(tetramethylene oxide)

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Abstract: Previously developed theoretical methods are used to calculate mean-square dipole moments of the poly(tetramethylene oxide) chain. Interactions between nonbonded atoms and groups in this chain are found to be either identical with or similar to interactions arising in polyethylene, polyoxymethylene, and polyoxyethylene. Statistical weights obtained in the analysis of the dimensions and dipole moments of these chains are thus applicable to the present investigation of the poly(tetramethylene oxide) chain. The calculated dipole moments are in good agreement with preliminary published results obtained on the undiluted, amorphous polymer by other workers. Values of the chain dimensions and the temperature coefficients of the dimensions and dipole moments are predicted.

Theoretical methods[1] found successful in the interpretation of the dipole moments of oxyethylene chains[2] are also applicable to poly(tetramethylene oxide), $-(\mathrm{CH_2{-}O{-}CH_2{-}CH_2{-}CH_2})-_x$. The energies associated with rotational states about skeletal bonds are required for the calculation of the statistical weights for all configurations of the chain as a whole. In the case of oxyethylene molecules, these energies had been estimated by previous analysis of the chain dimensions and their temperature coefficient.[3] Such information has not yet been obtained for tetramethylene oxide chains; the energies required can be reliably estimated, however, from published analyses of the configurations of other chain molecules of similar structure. These estimated energies, in conjunction with the C–O bond moment,[2] can be used to predict the *dipole moment ratio* $\langle\mu^2\rangle_0/nm^2$ of the mean-square dipole moment of the tetramethylene oxide chain unperturbed by long-range interactions, to the mean-square moment of the chain in the idealization that the skeletal bonds are freely jointed. The predicted value of this ratio in the asymptotic limit of long chain length can be compared with published experimental results.

In addition, it is possible to predict values of the chain dimensions and the temperature coefficients of both the dimensions and the dipole moments.

Theory

The Partition Function and Mean-Square Dipole Moment. The partition function Z of the poly(tetramethylene oxide) chain of degree of polymerization x (Figure 1) is

$$Z = \mathbf{J}^*\mathbf{U}_b\mathbf{U}_c\mathbf{U}_d\mathbf{U}_e(\mathbf{U}_a\mathbf{U}_b\mathbf{U}_c\mathbf{U}_d\mathbf{U}_e)^{x-2}\mathbf{U}_a\mathbf{U}_b\mathbf{U}_c\mathbf{U}_d\,\mathbf{J} \quad (1)$$

where $\mathbf{U}_a$ through $\mathbf{U}_e$, the rotational statistical weight matrices, refer to bonds such as $i-1$ through $i+3$, respectively. Definitions of all quantities in this equation, and in the following as well, have been given in the preceding paper[2] and apply here without change. The dipole moment ratio for this chain can be written

$$\langle\mu^2\rangle_0/nm^2 = 1 + (2/Znm^2)[1\ 0\cdots 0]\mathbf{G}_1\mathbf{G}_b\mathbf{G}_c\mathbf{G}_d\mathbf{G}_e\ \cdot$$
$$(\mathbf{G}_a\mathbf{G}_b\mathbf{G}_c\mathbf{G}_d\mathbf{G}_e)^{x-2}\mathbf{G}_a\mathbf{G}_b\mathbf{G}_c\mathbf{G}_d\begin{bmatrix} 0 \\ \vdots \\ \mathbf{J}\times\mathbf{m}_e \\ \mathbf{J} \end{bmatrix} \quad (2)$$

were $n = 5x$ is the number of skeletal bonds, and $m^2 = (m_a{}^2 + m_b{}^2 + m_c{}^2 + m_d{}^2 + m_e{}^2)/5$ is the average square of the bond moments.

Construction of Rotational Statistical Weight Matrices. In the rotational isomeric state model of the poly(tetramethylene oxide) chain, each skeletal bond is restricted to one of three states: the planar, *trans* (t) state for which the dihedral angle $\phi = 0°$, and two symmetrically disposed *gauche* ($g\pm$) states at $\phi = \pm 120°$. The statistical weight matrices required in eq 1 and 2 will be constructed in the usual manner,[1,2] utilizing distances between nonbonded atoms and groups in the assignment of rotational statistical weights. Distances pertinent to the present analysis are given in Table I.

Table I. Distances between Nonbonded Atoms and Groups and Statistical Weights

Conformation	Interacting atoms or groups	No. of bonds apart	Distance, A	Statistical wt
t_{i-1}	$\mathrm{CH_2\cdots CH_2}$	3	3.70	1
$g^{\pm}{}_{i-1}$		3	2.81	σ
$g^{\pm}{}_{i-2}\,g^{\pm}{}_{i-1}$	$\mathrm{CH_2\cdots CH_2}$	4	3.44	σ
$g^{\pm}{}_{i-2}\,g^{\mp}{}_{i-1}$		4	2.46	0
t_i	$\mathrm{CH_2\cdots CH_2}$	3	3.70	1
$g^{\pm}{}_i$		3	2.81	σ
$g^{\pm}{}_{i-1}\,g^{\pm}{}_i$	$\mathrm{CH_2\cdots CH_2}$	4	3.44	σ
$g^{\pm}{}_{i-1}\,g^{\mp}{}_i$		4	2.38	0
t_{i+1}	$\mathrm{O\cdots CH_2}$	3	3.77	1
$g^{\pm}{}_{i+1}$		3	2.90	σ'
$g^{\pm}{}_i\,g^{\pm}{}_{i+1}$	$\mathrm{CH_2\cdots CH_2}$	4	3.44	σ'
$g^{\pm}{}_i\,g^{\mp}{}_{i+1}$		4	2.46	0
t_{i+2}	$\mathrm{CH_2\cdots CH_2}$	3	3.86	1
$g^{\pm}{}_{i+2}$		3	2.95	σ''
$g^{\pm}{}_{i+1}\,g^{\pm}{}_{i+2}$	$\mathrm{O\cdots CH_2}$	4	3.50	σ''
$g^{\pm}{}_{i+1}\,g^{\mp}{}_{i+2}$		4	2.54	$\omega\sigma''$
t_{i+3}	$\mathrm{CH_2\cdots O}$	3	3.77	1
$g^{\pm}{}_{i+3}$		3	2.90	σ'
$g^{\pm}{}_{i+2}\,g^{\pm}{}_{i+3}$	$\mathrm{CH_2\cdots O}$	4	3.50	σ'
$g^{\pm}{}_{i+2}\,g^{\mp}{}_{i+3}$		4	2.54	$\omega\sigma'$

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[1] P. J. Flory, *Proc. Natl. Acad. Sci. U. S.*, **51**, 1060 (1964); P. J. Flory and R. L. Jernigan, *J. Chem. Phys.*, **42**, 3509 (1965).

[2] P. J. Flory and J. E. Mark, *J. Am. Chem. Soc.*, **88**, 3702 (1966).

[3] J. E. Mark and P. J. Flory, *ibid.*, **87**, 1415 (1965).

A rotation of ±120° about a CH_2–O bond such as $i-1$ of Figure 1 decreases the distance between two CH_2 groups separated by three bonds from a center-to-center distance of 3.70 to 2.81 A. Interactions arising from this "transition" are very nearly identical with those occurring in polyoxyethylene[2,3] and should give rise to a repulsive energy of approximately 900 cal $mole^{-1}$.[2] (This energy includes a coulombic contribution which is absent in the tetramethylene oxide chain; the small dipole moment of the C–O bond, however, indicates that this contribution should be quite small.[3]) *Gauche* states of either sign preceded by a *trans* state are therefore, assigned a statistical weight $\sigma = \exp(-900/RT)$ relative to a statistical weight of unity assigned to *trans* states irrespective of their predecessors. In the case of a *gauche* state preceded by a *gauche* state of like sign, no significant interactions would be expected between CH_2 groups separated by four bonds at a distance of 3.44 A, and thus g^+g^+ and g^-g^- states also receive statistical weights of σ. (This equivalence of $tg^\pm$ and $g^\pm g^\pm$ states was found to be a reasonable approximation for all skeletal bonds in the chain and will be used throughout the analysis of the statistical weight matrices.) Pairs of *gauche* states of opposite sign, however, place these CH_2 groups 2.46 A apart. Since the van der Waals radius of the CH_2 group is approximately 2.0 A,[4] steric repulsions must assuredly exclude such conformations. The resulting statistical weight matrix, formed by assigning row indices in the order t, g^+, g^- to states of bond $i-2$ and column indices in the same order to those of bond $i-1$, is

$$\mathbf{U}_a = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{bmatrix} \qquad (3)$$

Rotations about O–CH_2 bonds such as bond i give rise to essentially identical interactions, the only difference being the slightly closer approach of CH_2 groups in $g^\pm g^\mp$ rotational states. Therefore $\mathbf{U}_b = \mathbf{U}_a$.

The *trans*-to-*gauche* transition about a CH_2–CH_2 bond such as $i+1$ brings an O atom and CH_2 group separated by three bonds to a distance of separation of 2.90 A. Reference to the analysis[5] of the configuration of polyoxymethylene chains provides an indication of the energy change expected to accompany such a transition. A *gauche* rotation about any skeletal bond in the oxymethylene chain places an O atom with a small, negative charge 2.75 A from a CH_2 group carrying a positive charge of the same magnitude. Comparison of calculated[5] and experimental[6,7] values of the polyoxymethylene chain dimensions suggest a favorable energy of −1100 to −1400 cal $mole^{-1}$ for the *gauche* state relative to the *trans*. This energy arises primarily from dispersion forces, the coulombic contribution amounting to only a few hundred cal $mole^{-1}$.[5] Since the O atoms and CH_2 groups are significantly further apart in the comparable *gauche* conformation in poly(tetramethylene oxide), the favorable dispersion energy should be considerably smaller, perhaps negligibly small. In addition, steric repulsions should be absent at this distance of separation[5] and, because the CH_2 group is not positively charged, an appreciable coulombic contribution would not be expected. On the basis of this comparison an energy $E_{\sigma'}$ of 0 to −500 cal $mole^{-1}$ is indicated for the statistical weight $\sigma' = \exp(E_{\sigma'}/RT)$ assigned to these $g^\pm$ states. In $g^\pm g^\mp$ states repulsions between CH_2 groups separated by four bonds are again sufficiently large to assure exclusion of these conformations. Thus

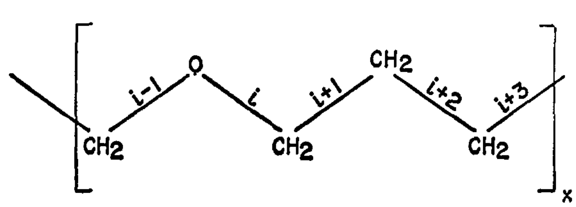

Figure 1. Enumeration of bonds in the poly(tetramethylene oxide) chain.

$$\mathbf{U}_c = \begin{bmatrix} 1 & \sigma' & \sigma' \\ 1 & \sigma' & 0 \\ 1 & 0 & \sigma' \end{bmatrix} \qquad (4)$$

A *gauche* rotation about a CH_2–CH_2 bond such as $i+2$ diminishes the distance between CH_2 groups separated by bonds $i+1$, $i+2$, and $i+3$ from 3.86 to 2.95 A. In polyethylene an energy of 400 (±100) cal $mole^{-1}$ was found[8] for the analogous *gauche* states, in which CH_2 groups are ~3.0 A apart. Since the energy associated with this rotation in the tetramethylene oxide chain may also include a small, positive coulombic contribution, the over-all energy may be slightly higher than that found in polyethylene; a value of approximately 500 cal $mole^{-1}$ would be a reasonable estimate. The statistical weight parameter for *gauche* states about these bonds is therefore $\sigma'' \cong \exp(-500/RT)$. *Gauche* rotations of opposite sign about bond pairs such as $i+1$ and $i+2$ place negatively charged O atoms 2.54 A from positively charged CH_2 groups. An almost identical situation arises in $g^\pm g^\mp$ states about CH_2–CH_2–O and O–CH_2–CH_2 bonds in polyoxyethylene;[3] the distance of separation of the O and CH_2 in this chain is 2.46 A. The energy contribution from these groups, separated by four bonds, was found to be approximately 340 cal $mole^{-1}$,[2,3] and thus a factor $\omega \cong \exp(-340/RT)$ is required for these states in the tetramethylene oxide chain. The completed matrix is

$$\mathbf{U}_d = \begin{bmatrix} 1 & \sigma'' & \sigma'' \\ 1 & \sigma'' & \omega\sigma'' \\ 1 & \omega\sigma'' & \sigma'' \end{bmatrix} \qquad (5)$$

Interactions between CH_2 groups and O atoms brought about by a *gauche* rotation about CH_2–CH_2 bonds such as $i+3$ are identical with those occurring about CH_2–CH_2 bonds such as $i+1$. Similarly, interactions between groups separated by four bonds in $g^\pm g^\mp$ conformations are the same as those found for the same pairs of rotational states about bonds $i+1$ and $i+2$. The appropriate matrix can therefore be

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(4) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960; A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(5) P. J. Flory and J. E. Mark, *Makromol. Chem.*, **75**, 11 (1964).

(6) V. Kokle and F. W. Billmeyer, Jr., *J. Polymer Sci.*, **B3**, 47 (1965).

(7) W. H. Stockmayer and L.-L. Chan, *ibid.*, (A-2)4, 437 (1966).

(8) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Am. Chem. Soc.*, **88**, 631 (1966).

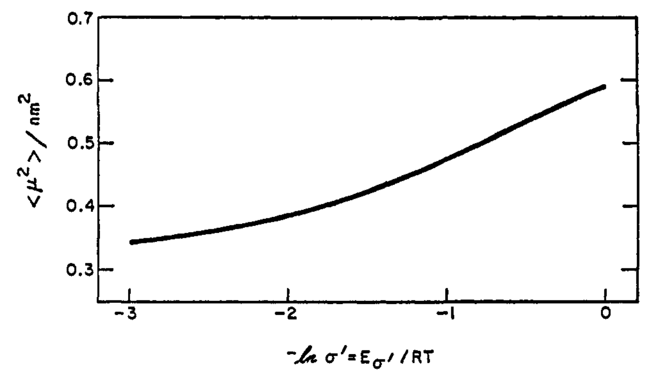

Figure 2. The dipole moment ratio as a function of ln σ' for σ = 0.215, σ'' = 0.426, and ω = 0.563.

written immediately

$$\mathbf{U}_e = \begin{bmatrix} 1 & \sigma' & \sigma' \\ 1 & \sigma' & \omega\sigma' \\ 1 & \omega\sigma' & \sigma' \end{bmatrix} \qquad (6)$$

Finally, the matrix $\mathbf{U}_l$ required in $\mathbf{G}_l$ appearing in eq 2 is simply the 3 by 3 unit matrix $\mathbf{E}_3$.

Comparison of Theory and Experiment

Values of $\langle\mu^2\rangle_0/nm^2$ were calculated using bond moments $m_{C-O} = -m_{O-C} = 0.99$ and $m_{C-C} = 0.0$ D.,[2] bond angle supplements of $\theta = 70°$ for all skeletal bonds,[2,3] a degree of polymerization $x = 120$, and statistical weight parameters appropriate for 20°, the temperature at which the dipole moment of poly(tetramethylene oxide) has been measured.[9] Values of the parameters were $\sigma = \exp(-900/RT) = 0.215$, $\sigma'' = \exp(-500/RT) = 0.426$, and $\omega = \exp(-340/RT$ 0.563. Although σ' should be in the range 1 to 2.35 on the basis of the expected energy $E_{\sigma'} \cong 0$ to -500 cal mole^{-1}, considerably larger values of σ' were included for illustrative purposes. For reasons given above, values of $\sigma' < 1$ are not physically realistic and therefore are not considered here. Figure 2 shows the dependence of the dipole moment ratio on $-\ln \sigma'$. For the anticipated range of $E_{\sigma'}$, $\langle\mu^2\rangle_0/nm^2 = 0.5$ to 0.6 is predicted.

In a recent experimental study,[9] the mean-square dipole moment of poly(tetramethylene oxide) was estimated from dielectric constant measurements at 20° on an undiluted, amorphous sample having a degree of polymerization of several thousand on the basis of its weight-average molecular weight. The difference between the degree of polymerization used in the calculation and that of the polymer sample studied is of no consequence since $\langle\mu^2\rangle_0/nm^2$ is assuredly well within 1% of its asymptotic limit $[\langle\mu^2\rangle_0/nm^2]_{n\to\infty}$ at $x = 120$.[2] Poly(tetramethylene oxide) is normally crystalline below $T_m = 38°$; the measurements considered here, however, were made on a quenched sample described as wholly amorphous.[9] There is now much evidence that long-range interactions do not have a significant effect on the configuration adopted by a long-chain molecule in the bulk, amorphous state.[10] Thus, the reported experimental results refer to the molecules essentially in their unperturbed state and qualify as an approximate test of the calculations described above. Furthermore, since long-range interactions do not affect the dipole moment of this chain,[2] the subscript on $\langle\mu^2\rangle_0$ will henceforth be deleted.

The data yield $\langle\mu^2\rangle/nm^2 = 0.53$ to 0.64,[11] the wide range reflecting the difficulty in obtaining a value of the limiting high-frequency dielectric constant of the bulk polymer sample. In addition, undetected crystallinity could greatly affect these results, decreasing the dipole moment ratio below its true value. Nonetheless, these values are in excellent agreement with the range 0.5 to 0.6 predicted for this ratio. On the basis of the calculated results of Figure 2, a reasonable estimate of the probable error in the experimental value, and the lack of any physical justification for considering the range $\sigma' < 1$, it can be stated with confidence that σ' should have a value between approximately 1 and 2, the corresponding energy at 20° being 0 to -400 cal mole^{-1}.

The complete set of parameters ($\sigma = 0.215$, $\sigma' = 1$ to 2, $\sigma'' = 0.426$, and $\omega = 0.563$), the bond dipole moments given above, and the bond lengths $l_{C-C} = 1.53$ A and $l_{C-O} = 1.43$ A[12] can be used to calculate the *characteristic ratio* $\langle r^2\rangle_0/nl^2$ of the chain dimensions and the temperature coefficient[2] of both $\langle r^2\rangle_0$ and $\langle\mu^2\rangle$. Values thus calculated for 20° are $\langle r^2\rangle_0/nl^2 = 5.3$ to 4.6,[13] $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = -1.3$ to -1.2×10^{-3} deg^{-1}, and $\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T = 1.0$ to 1.5×10^{-3} deg^{-1}.

Discussion

Although this model of the poly(tetramethylene oxide) chain has been evaluated using only tentative experimental results, the following general features seem to be reliably established: (i) for rotations about CH_2–O and O–CH_2 bonds, and about CH_2–CH_2 bonds which bring CH_2 groups into apposition, *gauche* states are of significantly higher energy than *trans;* (ii) in the case of rotations about CH_2–CH_2 bonds which bring O atoms and CH_2 groups into proximity, either free rotation occurs or the *gauche* state is of slightly lower energy than the *trans;* and (iii) $g^{\pm}g^{\mp}$ conformations in which two CH_2 groups separated by four bonds are brought into steric conflict are excluded, but similar conformations in which O atoms and CH_2 groups conflict are only suppressed.

The calculated partial derivatives of $\langle r^2\rangle_0$ and $\langle\mu^2\rangle$ with respect to each of the statistical weight parameters can be used to provide a qualitative interpretation of the predicted values of $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ and $\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T$. As in the case of oxyethylene chains, *trans*-to-*gauche* transitions generally decrease $\langle r^2\rangle_0$ but increase $\langle\mu^2\rangle$ since for the all-*trans* form[2]

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[9] R. E. Wetton and G. Williams, *Trans. Faraday Soc.*, **61**, 2132 (1965).

[10] P. J. Flory in "Lectures in Material Science," P. Leurgens, Ed., W. A. Benjamin, Inc., New York, N. Y., 1963.

[11] The analysis[9] of these results in terms of a chain model [B. E. Read, *Trans. Faraday Soc.*, **61**, 2140 (1965)] which ignores the interdependence of bond rotational states and employs only one "average" statistical weight to characterize the three markedly different *trans*-to-*gauche* transitions discussed above obviously is incorrect.

[12] H. J. M. Bowen and L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1958.

[13] M. Kurata, H. Utiyama, and K. Kamada [*Makromol. Chem.*, **88**, 281 (1965)] have reported molecular weights, intrinsic viscosities, and second virial coefficients of tetramethylene oxide polymers of narrow molecular weight distribution in ethyl acetate at 30°. Treatment of these data to account for long-range interactions [T. A. Orofino and P. J. Flory, *J. Chem. Phys.*, **26**, 1067 (1957)] yields a value of $\langle r^2\rangle_0/nl^2 = 4.8 \pm 0.3$.

$$\lim_{n \to \infty} \langle r^2 \rangle_0 / nl^2 = \infty \text{ and } \lim_{n \to \infty} \langle \mu^2 \rangle n / m^2 = 0$$

An increase in temperature increases the *gauche* population about bonds such as $i - 1$, i, and $i + 2$ in Figure 1, but either leaves unchanged or decreases the *gauche* population about bonds such as $i + 1$ and $i + 3$. The former effect predominates, giving rise to a negative temperature coefficient of $\langle r^2 \rangle_0$, which is increased in magnitude by the concomitant increase in population of compact $g^{\pm}g^{\mp}$ states about some bond pairs in the chain. The molecular basis for the increase in $\langle \mu^2 \rangle$ with temperature is more difficult to visualize, but the primary effect is the increase in the number of *gauche* states about bonds such as $i - 1$, i, and $i + 2$ as the temperature is raised.

According to this general analysis, the form of the poly(tetramethylene oxide) chain of minimum *intra*molecular energy is ($ttg^{\pm}tg^{\pm}$), where the bonds in the repeat unit are designated in the order given in Figure 1. The intramolecular energy difference between this form and the planar zigzag (*ttttt*) conformation is small, however, or possibly zero. The all-*trans* form of the chain would be more efficiently packed into a crystalline lattice than would the ($ttg^{\pm}tg^{\pm}$) form, which apparently represents an unusual helical arrangement having a large number of monomer units per turn of the helix. X-Ray diffraction studies[14] on this polymer show that the chains are in the all-*trans* conformation in the crystalline lattice, thus indicating the *inter*molecular interactions may be of importance when two or more forms of the chain are of low, and approximately equal, intramolecular energies.

Although the theoretical calculations are in good agreement with the dipole moment obtained on poly(tetramethylene oxide) chains in the bulk, amorphous state, considerably more experimental results are required for a thorough evaluation of the model. Of particular importance would be determinations of $\langle r^2 \rangle_0 / nl^2$ and $\langle \mu^2 \rangle / nm^2$ for the chain in dilute solution; the temperature coefficient of both of these quantities and the dependence of $\langle \mu^2 \rangle / nm^2$ on chain length are also of obvious interest.

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[14] H. Tadokoro, Y. Chatani, M. Kobayashi, T. Yoshihara, and S. Murahashi, *Progr. Polymer Phys., Japan*, **6**, 303 (1964).

An Electron Spin Resonance Study of the Reduction of Polynitromesitylenes and -durenes[1,2]

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Abstract: Bernal and Fraenkel have reported a series of unidentified free radicals obtained by electrolytic reduction of trinitromesitylene, dinitromesitylene, and dinitrodurene. These radicals are shown to be nitroamine anions corresponding to the reduction of one nitro group. Complete analysis of the proton hyperfine structure observed in the esr spectra is reported. The reduction reactions of *m*- and *p*-dinitrobenzene and the spectra of the *m*- and *p*-nitroaniline anions are reported for comparison. Unidentified radicals were detected on reduction of trinitro-, aminodinitro-, and dinitromesitylene as well as dinitroisodurene. These radicals are apparently due to side reactions, the nature of which is discussed. A mechanism for the observed reduction of dinitrodurene to the diaminodurene cation is proposed. A correlation of the spin-density distribution in hindered nitrobenzenes with polarographic half-wave potentials is presented.

In recent years, electron spin resonance (esr) has proved to be a useful tool in characterizing the reactions of aromatic radical ions in solution. Numerous examples of substitution, rearrangement, and elimination reactions have been found by this technique.[4] In an investigation of the esr spectra of several polynitro aromatic anions, Bernal and Fraenkel[5] found that by electrolyzing solutions at potentials more negative than those used to produce the monoanions, new paramagnetic species were formed which had fewer equivalent nitro groups than the starting material. These radicals were apparently not simple elimination or rearrangement products, since, for example, the second radical obtained from reduction of dinitrodurene is not the nitrodurene anion,[5] nor, as we shall show, is it the nitroisodurene or pentamethylnitrobenzene anion.

Qualitatively, these results are similar to those of Ward[6] who prepared polynitromesitylene radicals by chemical reduction in dimethoxyethane solution and observed a hyperfine splitting from a single nitrogen nucleus. Ward suggested that his results indicated a tight ion pair such that an alkali metal ion traps the spin density on a single nitro group. This interpreta-

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[2] Supported in part by a grant from the National Science Foundation and by the ARPA program at Brown University.

[3] Du Pont Teaching Fellow, 1964–1965.

[4] R. N. Adams, *J. Electronanal. Chem.*, **8**, 151 (1964).

[5] I. Bernal and G. K. Fraenkel, *J. Am. Chem. Soc.*, **86**, 1671 (1964).

[6] R. L. Ward, *J. Chem. Phys.*, **32**, 410 (1960); *J. Am. Chem. Soc.*, **83**, 1296 (1961).