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Modulus and Orientation of the Dipole Moment Associated with the Side Group of Poly(*N*-((vinyloxy)carbonyl)carbazole)[§]

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Abstract: The mean-square dipole moments $\langle \mu^2 \rangle$ of *N*-carbethoxycarbazole and 2,2′-oxydi-*N*-carbethoxycarbazole, two low molecular weight models of poly(*N*-((vinyloxy)carbonyl)carbazole), were measured in solutions of the compounds in dioxane at several temperatures between 30 and 60 °C. The experimental values of $\langle \mu^2 \rangle$ at 30 °C amounted to 3.82 and 7.46 D^2 for the former and latter models, respectively. The analysis of the dipole moment of *N*-carbethoxycarbazole suggests that the orientation of this vector forms an angle of 46 ± 8° with the N–CO bond. Moreover, the critical interpretation of the dipole moment of 2,2′-oxydi-*N*-carbethoxycarbazole by using the rotational states model indicates that good agreement between theory and experiment can be obtained assuming that the preferred orientation of the side group is ±45° relative to the lateral C–H bond of the compound in the planar all-trans conformation.

Owing to the technological importance of poly(*N*-vinylcarbazole) (PVCA) as a photoconductor, the investigation of polymers based on *N*-vinylcarbazole has become a flourishing type of research.[1] The substitution of some of the hydrogen atoms of the carbazole group for other atoms or atomic groups may affect the photoconductance properties of the resulting polymer. In this sense it has been reported that the bromination[2] and nitration[1] of the carbazolyl group enhances the conductance o the polymer chains.

Other investigations have also focused on the study of the photophysical activity of carbazolyl-containing polymers in which the carbazolyl group is not directly bonded to the skeletal bonds of the main chain, but is instead more than one atom removed from the backbone carbon atom.[3] In the case of poly(*N*-(vinyloxy)carbonyl)carbazole) (PFCZ), for example, the carbazolyl nitrogen is bonded to the chain through a carboxylate group which confers on the carbazolyl group a steric freedom greater than it enjoys in PVCA. The effect on dielectric properties of substitution at the nitrogen atoms may be rather significant owing to inductive effects between the carbazolyl and carboxylate groups. With the aim of analyzing these effects, we have measured in the present work the dipole moment of *N*-carbethoxycarbazole (NCEC), the monomer analogue of PFCZ, whose structure is shown in Figure 1. The orientation of the dipole moment was determined by measuring the dipole moment of 2,2′-oxydi-*N*-carbethoxycarbazole (ODNCEC) (Figure 2) and further critical interpretation of the experimental result by using statistical mechanics procedures. The results obtained may be used to predict the polarity of PFCZ chains.

Experimental Section

Synthesis of the Compounds. The monomeric model compound NCEC was prepared by reaction of carbazole with ethyl chloroformate with use of phase transfer catalysis as described previously.[3]

In the preparation of the dimeric model compound ODNCEC, 2,2′-oxydiethylchloroformate (Sociêté Nationale des Foudres et Explosifs), carbazole (Fluka), tetrabutylammonium hydrogen sulfate (TBAH) (Aldrich Chemical Co.), and methylene chloride were used without further purification. A solution of 0.01 mol of 2,2′-oxydiethyl chloroformate in 50 mL of CH_2Cl_2 was added under nitrogen to a stirred mixture of 0.02 mol of carbazole, 10^{-3} mol of TBAH catalyst, 2 mL of 50% aqueous NaOH, and 70 mL of CH_2Cl_2 at room temperature. After 2 h the reaction mixture was filtered and washed with water. The organic layer was dried with $CaCl_2$. The crude product was obtained after evaporation of the solvent and was purified by recrystallization from ethanol (mp 119–120 °C). The yield of the purified dimeric compound was 60%. Anal. Calcd for $C_{30}H_{24}N_2O_5$: C, 73.17; H, 4.88; N, 5.69; O, 16.26. Found: C, 73.08; H, 4.81; N, 5.46; O, 16.65.

Table I. Summary of Dielectric Results

	T, °C			
	30	40	50	60
	N-Carbethoxycarbazole			
$d(\epsilon - \epsilon_1)/dw$	2.406	2.304	2.212	2.111
$d(n^2 - n_1^2)/dw$	0.480	0.474	0.470	0.467
$\langle \mu^2 \rangle$, D^2	3.82_3	3.82_5	3.83_0	3.80_0
	2,2′-Oxydi-*N*-carbethoxycarbazole			
$d(\epsilon - \epsilon_1)/dw$	2.345	2.249	2.153	2.064
$d(n^2 - n_1^2)/dw$	0.520	0.518	0.519	0.519
$\langle \mu^2 \rangle$, D^2	7.45_7	7.44_7	7.39_3	7.35_0

^{1}H NMR ($CDCl_3$; reference Me_4Si) δ 8.25 (4 H, d, H_c), 7.86 (4 H, ddd, H_f), 7.35 (4 H, td, H_d), 7.24 (4 H, td, H_e) (J_{ortho} = 7.5 Hz, J_{meta} = 1.5 Hz, J_{para} = 0.7 Hz); δ 4.74 (4 H, m, H_b), 4.05 (4 H, m, H_a).

Dielectric Experiments. Dielectric measurements were carried out on solutions of the compounds in dioxane. Since the principal impurities in *p*-dioxane are water, acetic acid, and glycol acetal, the solvent was refluxed for 48 h with potassium hydroxide and then was separated and refluxed with phenyl isocyanate[4] for 24 h. Finally it was carefully distilled in a fractionation column of about 20 theoretical plates and was used in the dielectric measurements immediately after its purification.

The dielectric constants of the solutions and of the solvent were measured with a capacitance bridge (General Radio, type 1620 A) operating at a frequency of 10 kHz. The three-terminal cell[5] was calibrated at 30, 40, 50, and 60 °C with benzene (Merck), cyclohexane (Merck), and carbon tetrachloride (Merck). The solvents had a purity exceeding 99.5% as received and were further purified with Linde Type 4A molecular sieves. Values of the increments of the index of refraction of the solutions with respect to the solvent were measured with a He-Ne KMX-16 laser differential refractometer (Chromatix Inc., USA) operating at 632.8 nm.

Dielectric Results

Values of the mean-square dipole moment $\langle \mu^2 \rangle$ were calculated by the method of Guggenheim and Smith[6,7] which results in the equation

$$\langle \mu^2 \rangle = (27kTM/4\pi\rho N_A(\epsilon_1 + 2)^2)\,((d(\epsilon - \epsilon_1)/dw) - d(n^2 - n_1^2)/dw) \qquad (1)$$

where k is the Boltzmann constant, T is the absolute temperature, M is the molecular weight of the solute, N_A is Avogadro's number,

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[§] This paper is dedicated to Prof. J. Ocon on the occasion of his 65th birthday.

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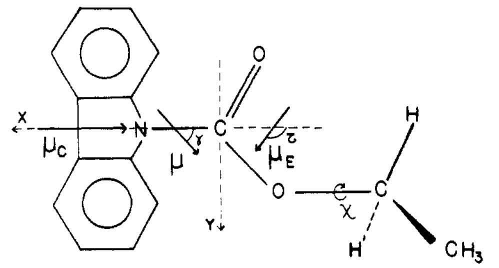

Figure 1. Structure of the *N*-carbethoxycarbazole molecule. The positive direction of the dipole moment of the whole molecule (μ) and the carbazole (μ_c) and ester (μ_e) groups are indicated by arrows.

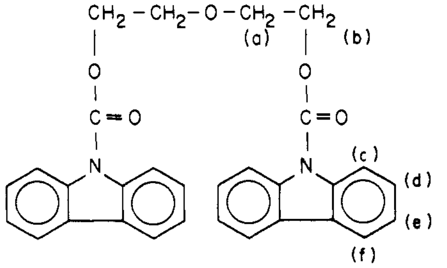

Figure 2. Structure of 2,2′-oxydi-*N*-carbethoxycarbazole. The chemical shifts of the a, b, c, d, e, and f protons are indicated in the text.

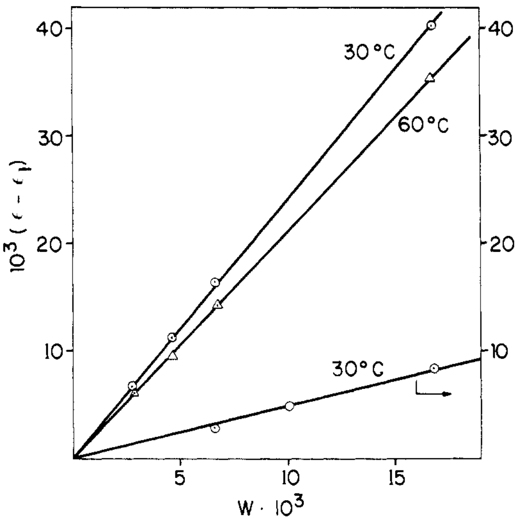

Figure 3. Increments in dielectric constant and squared index of refraction for solutions of *N*-carbethoxycarbazole in dioxane.

and ρ is the density of the solvent; ϵ and n are the dielectric constant and index of refraction of the solution, respectively, and ϵ_1 and n_1 represent the same quantities for the solvent. Values of the required derivatives $d(\epsilon - \epsilon_1)/dw$ and $d(n^2 - n_1^2)/dw$ were determined from plots of the dielectric increments $\Delta\epsilon = \epsilon - \epsilon_1$ and $\Delta n^2 = n^2 - n_1^2$ against the weight fraction w of the solute. Typical plots of this kind are given in Figures 3 and 4 for NCEC and ODNCEC at 30 and 60 °C, and the values of the two derivatives for 30, 40, 50, and 60 °C are given in Table I. Values of the mean-square dipole moment at the temperatures of interest are shown in the third and sixth rows of Table I for NCEC and ODNCEC, respectively; the uncertainty of these values was estimated to be ca. 5%.

The dipole moment of NCEC does not show a noticeable temperature dependence. However, the dipole moment of ODNCEC seems to decrease as the temperature increases. The value of the temperature coefficient $d \ln\langle\mu^2\rangle/dT$, estimated from the slope of the plot of the natural logarithm of the mean-square dipole moment against temperature, amounts to -5.0×10^{-4} K^{-1}.

Theoretical Analysis

Dipole Moment of *N*-Carbethoxycarbazole. Figure 1 shows the structure of the molecule in the conformation in which both the carbazole and the ester groups are coplanar. The dipole moment of this molecule, μ, can be considered as the sum of the two contributions: μ_c due to the carbazole ring and μ_e from the ester group; the positive directions of these two vectors are represented by arrows in Figure 1.

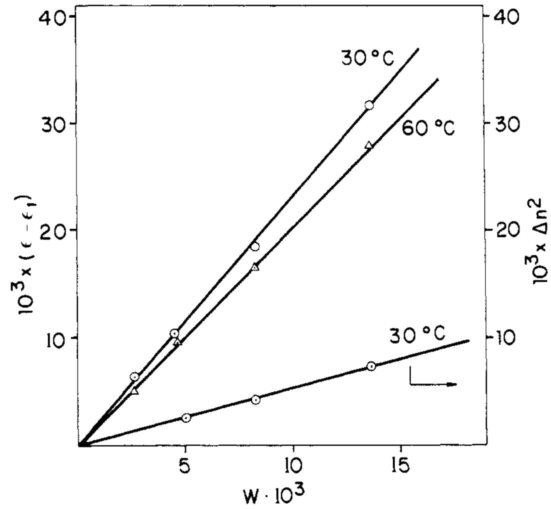

Figure 4. Typical data showing the concentration dependent of the increments in dielectric constant and squared index of refraction for solutions of 2,2′-oxydi-*N*-carbethoxycarbazole in dioxane.

Due to the symmetry of the carbazole group, μ_c should lie along the N–CO bond and, consequently, the possible rotation of the group around that bond is irrelevant for the present analysis. The modulus of μ_c was assumed to be that of *N*-isopropylcarbazole[8] which is 2.93 D. A value of 1.84 D, reported as the dipole moment of ethyl acetate,[9,10] was used for the modulus of μ_e. The direction of this vector is determined by the angle that it makes with the direction of the N–CO bond (see Figure 1); according to Flory and co-workers,[11] $\tau = 123°$.

The components of μ, referred to the coordinate system shown in Figure 1, can be written as

$$\mu_x = -\mu_c + \mu_e \cos(180 - \tau) \qquad \mu_y = \mu_e \sin(180 - \tau) \qquad \mu_z = 0 \tag{2}$$

By using the values indicated above for the three parameters, the resulting μ vector has a modulus of 2.47 D and a direction defined by $\gamma = 38.7°$. The disagreement between the experimental value of $(\langle\mu^2\rangle)^{1/2} = 1.955$ reported in the Experimental Section and the result of this simple calculation indicates that there are strong inductive effects between the dipole moments of the two polar groups of the molecule, in the sense that each of these groups modifies the charge distribution of the other one.

There are two simple ways in which these inductive effects can be taken into account: either diminishing the value of μ_c or increasing the angle τ until the value of μ calculated according to eq 2 agrees with the experimental result.[12] Let us examine each one of these options. According to eq 2, if we keep constant the values of μ_e and τ, a value of $\mu_c = 2.20$ D is needed in order to bring agreement between theoretical and experimental results of μ; the orientation of the resulting vector would then be defined by $\gamma = 52.2°$. On the other hand, if we keep constant μ_c and μ_e, agreement between theory and experiment is achieved with $\tau = 139.4°$, giving $\gamma = 38.0°$. Of course, there are many combinations of these three parameters that produce a dipole moment in agreement with the experimental result (for instance $\mu_c = 2.5$;

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[12] However, modification of μ_e while keeping τ and μ_c constant does not produce agreement between theoretical and experimental values of μ, since the absolute value of μ_x decreases as μ_e increases, while μ_y increases with increasing μ_e, so that the resulting μ is always larger than the experimental value.

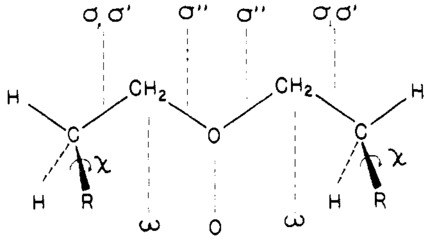

Figure 5. The molecule of 2,2′-oxydi-*N*-carbmethoxycarbazole in all-trans conformation. R represents the side group. The angle χ measures the rotation of the side group over the O–C bond; the value of $\chi = 0$ is assigned to the position in which the carbonyl bond C=O is cis to the lateral H–C bond (as represented in Figure 1). First/second order statistical weights are shown above/below the skeleton of the molecule.

$\mu_c = 2.0$; $\tau = 130.0°$ that gives $\gamma = 51.6°$). Moreover, it is very unlikely that the inductive effects between these two dipole moments would be restricted to modify only one of the parameters. However, if we admit that the inductive effects produce only small modifications on the dipole moments of the two polar groups and the dipole moment of the whole molecule (obtained by addition of the two contributions from the polar groups) should have a modulus which agrees with the experimental result, it seems reasonable to assume that the orientation (given by the angle γ) should lie in the interval determined by the two simple options examined above. Consequently, we will use a dipole moment of $\mu = 1.955$ D with an orientation defined by $\gamma = 46 \pm 8°$ for the molecule of NCEC.

Since the dipole moment μ does not depend on any rotational angle, the only mechanism through which it can change with temperature is the modification of bond lengths and bond angles. At the low temperatures used for the experimental measurements, the modifications of bond lengths are negligible and the variations of bond angles should be very small. Therefore, this simple analysis suggests that μ should be very insensitive to the temperature, in good agreement with the small value of the temperature coefficient obtained in the Experimental Section.

Dipole Moment of 2,2′-Oxydi-*N*-carbethoxycarbazole. The structure of the molecules is shown in Figure 5 with the skeleton having the planar all-trans conformation. In this figure R represents the carbazole group whose orientation is governed by the rotation χ around the O–C bond; the value of $\chi = 0$ is assigned to the position in which the carbonyl bond O=C is cis to the lateral H–C bond (as represented in Figure 1).

Standard methods of matrix multiplication[13,14] usually employed for chain molecules, can be applied to calculate the mean-square dipole moment of the ODNCEC molecule. For the present calculation, all the valence angles of the skeleton were assumed to be 110° and the rotational isomers t, g± were located at 0, ±120°, respectively. Four statistical weight matrices, each representing one of the four bonds of the skeleton, are required for the calculations. Following standard procedures, the following matrices can be formulated

$$\mathbf{U}(\mathrm{C{-}CH_2}) = \begin{bmatrix} 1 & \sigma & \sigma' \\ 1 & \sigma & \sigma' \\ 1 & \sigma & \sigma' \end{bmatrix}; \quad \mathbf{U}(\mathrm{CH_2{-}O}) = \begin{bmatrix} 1 & \sigma''\omega & \sigma'' \\ 1 & \sigma'' & \sigma'' \\ 1 & \sigma'' & \sigma''\omega \end{bmatrix}$$

$$\mathbf{U}(\mathrm{O{-}CH_2}) = \begin{bmatrix} 1 & \sigma'' & \sigma''\omega \\ 1 & \sigma'' & 0 \\ 1 & 0 & \sigma''\omega \end{bmatrix}; \quad \mathbf{U}(\mathrm{CH_2{-}C}) = \begin{bmatrix} 1 & \sigma' & \sigma \\ 1 & \sigma' & \sigma \\ 1 & \sigma' & \sigma \end{bmatrix}$$

where each statistical weight is assumed to be a single Boltzmann exponential of its corresponding conformational energy.

The two statistical weights σ and σ' appearing in U(C–CH$_2$) should be close to unity since the strongest interaction produced by rotation over this bond is the O···R which does not change appreciably from t to g$^+$ or g$^-$ rotational states. Conformational energy calculations, performed with a 6-12 Lennard-Jones function to represent nonbonded potentials[11,15] and partial charges for dipole–dipole interactions,[16] resulted in an energy difference between these three rotational isomers (i.e., t, g±) of ca. 0.15 kcal mol^{-1}, a value which is within the estimated inaccuracy of this kind of calculations. Consequently, we have used E_σ and $E_{\sigma'}$ as adjustable parameters in the range ±0.2 kcal mol^{-1} (see below). By symmetry, the statistical weight matrix for the CH$_2$–C bond can be obtained by interchanging the second and third columns of U(C–CH$_2$).

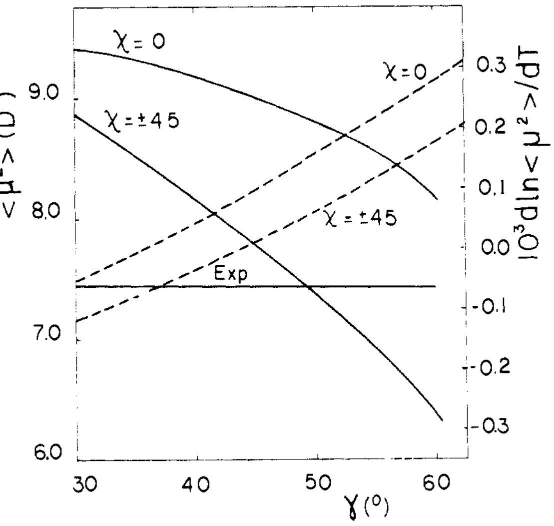

Figure 6. Dependence of the mean-square dipole moment (solid lines) and its temperature coefficient (dashed lines) of 2,2′-oxydi-*N*-carbethoxycarbazole on the angles γ and χ. The angle γ governs the orientation of the dipole moment of the side group whereas χ represents the rotation of the whole side group over the O–C bond. Calculations were performed at 30 °C with $E_\sigma = E_{\sigma'} = 0$, $E_{\sigma''} = 1.0$, and $E_\omega = 2.1$ kcal mol^{-1}.

Bonds CH$_2$–O and O–CH$_2$ are typical of polyoxides. Values of $E_{\sigma''} = 0.9$ to 1.2 kcal mol^{-1} have been used to represent the first-order energy of g± vs. t states of these bonds.[17-20] In the present analysis, we have used $E_{\sigma''} = 1.0$ kcal mol^{-1} without any optimization since, as will be shown below, the value of $\langle\mu^2\rangle$ is insensitive to this energy. The factor ω appearing in tg and g$^+$g$^-$ conformations of U(CH$_2$–O) and tg$^-$, g$^-$g$^-$ states of U(O–CH$_2$) is due to the R···CH$_2$ interaction; a value of $E_\omega = 2.1$ kcal mol^{-1} was used for these interactions.[18,19] Conformations g$^+$g$^-$ and g$^-$g$^+$ in U(O–CH$_2$) give rise to very strong R···R interactions, thus a statistical weight of zero was assigned to these conformations.

Two dipole moments, each having a magnitude of 1.07 D and the direction of the O–CH$_2$ bonds, were assigned to the ether part of the molecule.[16,21,22] The dipole moment of each R group was assumed to have a modulus of 1.95 D and a direction defined by the γ angle (see Figure 1). Standard procedures were used to write the components of these two vectors in the coordinate system affixed to the next bond of the skeleton[13,14] (i.e., bonds C–CH$_2$ and C–H for the first and second groups, respectively). The resulting components (and the value of $\langle\mu^2\rangle$ for the whole molecule) depend on the value assigned to the χ angle. Thus, taking $\chi = 0$ and $\gamma = 46°$, these components are −0.095, 0.141, 1.948. However, the preferred orientations for the acetate group are given by[11,23] $\chi = \pm 45°$; with positive and negative values of this angle equally weighted, the components of μ are 0.073, −0.109, and 1.736 for $\gamma = 46°$.

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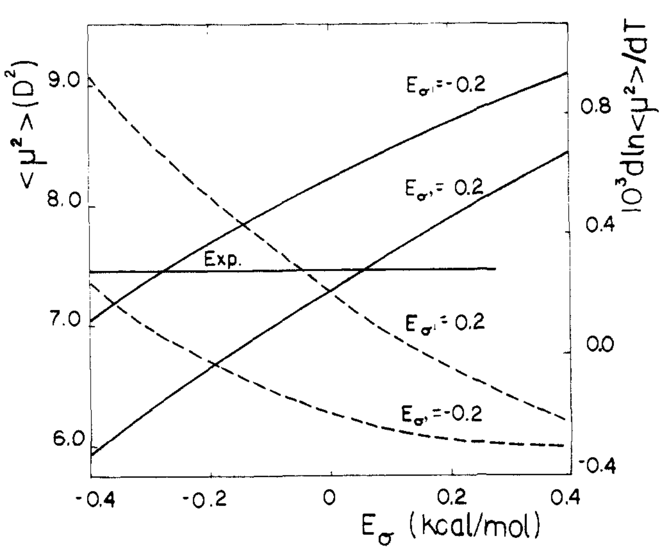

Figure 7. Dependence of the mean-square dipole moment (solid lines) and its temperature coefficient (dashed lines) of 2,2′-oxydi-*N*-carbethoxycarbazole on the conformational energies E_σ and $E_{\sigma'}$. Calculations were performed at 30 °C with $E_{\sigma''}$ = 1.0 and E_ω = 2.1 kcal mol^{-1}; γ = 46° and χ = ±45°.

Values of $\langle \mu^2 \rangle$ and its temperature coefficient are respectively represented as solid and dashed lines in Figures 6 and 7. Figure 6 shows the variation of these two magnitudes with the χ and γ angles, computed at 30 °C with $E_\sigma = E_{\sigma'} = 0$, $E_{\sigma''} = 1.0$, and E_ω = 2.1 kcal mol^{-1}. As this figure shows, exact agreement between theoretical and experimental values of $\langle \mu^2 \rangle$ is obtained with γ = 50° if the preferred orientations χ = ±45° are used, while to achieve this agreement with χ = 0 would require $\gamma \simeq 70°$ which is out of the range determined from the analysis of the NCEC molecule (see above). However, with γ = 50° and χ = ±45°, the theoretical value of the temperature coefficient of $\langle \mu^2 \rangle$ is roughly 0, in contrast with the small negative result shown in the Experimental Section.

Figure 7 shows the variation of $\langle \mu^2 \rangle$ and d ln $\langle \mu^2 \rangle$/dT with the conformational energies E_σ and $E_{\sigma'}$, calculated with T = 30 °C, γ = 46°, χ = ±45°, $E_{\sigma''}$ = 1.0, and E_ω = 2.1 kcal mol^{-1}. As this figure indicates, the calculated value of $\langle \mu^2 \rangle$ agrees with the experimental results when $E_\sigma = -0.1 \pm 0.1$ and $E_{\sigma'} = 0.1 \pm 0.1$ kcal mol^{-1}, in good concordance with the results of conformational energy calculations (see above). The agreement between theory and experiment is not so satisfactory in the case of d ln $\langle \mu^2 \rangle$/dT. Thus, a slightly positive value of this magnitude is suggested by Figure 7 whereas a negative value was found in the Experimental Section.

The calculated values of $\langle \mu^2 \rangle$ are insensitive to the conformational energies $E_{\sigma''}$ and E_ω. Thus, variations of 1 kcal mol^{-1} in $E_{\sigma''}$ and E_ω produce respectively modifications of 0.6% and 0.1% in $\langle \mu^2 \rangle$. Consequently, the effect of these two conformational energies on d ln $\langle \mu^2 \rangle$/dT is also negligible.

In view of the foregoing analysis, we conclude that is is possible to obtain excellent agreement between theoretical and experimental values of $\langle \mu^2 \rangle$ for the ODNCEC molecule using a reasonable set of parameters. However, the agreement is much poorer in the case of d ln $\langle \mu^2 \rangle$/dT, although this discrepancy could be in part due to the experimental error involved in the determination of a temperature coefficient. It should be pointed out in this regard that the temperature coefficients are in general relatively small quantities corresponding to changes of only a few tenths of a percent per degree. Consequently, they are difficult to determine with accuracy.

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Registry No. PFCZ, 104911-59-3; NCEC, 24650-61-1; ODNCEC, 104911-57-1; 2,2′-oxydiethyl chloroformate, 106-75-2; carbazole, 86-74-8.

Communications to the Editor

Photochemical Reductive Elimination of Hexaazido Complexes of Tin(IV) and Lead(IV)

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The discussion of the photochemistry of coordination compounds is almost exclusively restricted to complexes of transition metals.[1] Although some scattered observations on the light sensitivity of coordination compounds of main-group metals have been reported, this important aspect of inorganic photochemistry has been largely ignored.[2] A general concept which relates characteristic excited states to typical reactions does not yet exist for complexes of main-group metals. Systematic investigations in this field are also of interest with regard to technical applications.[3] To some degree the lack of knowledge of this part of inorganic photochemistry seems to be related to the kinetic lability of complexes of main-group metals. In many cases well-defined compounds do not exist in solution, particularly in water. However, in organic solvents which are weakly coordinating many main-group metal complexes dissolve without decomposition and are thus susceptible to detailed photochemical studies. We report here our observations of an efficient photochemical reductive elimination of the complex ions $[Sn(N_3)_6]^{2-}$ and $[Pb(N_3)_6]^{2-}$ in acetonitrile. The photolysis leads to the formation of Sn(II) or Pb(II) and molecular nitrogen.

The compounds $[(C_4H_9)_4N]_2[Sn(N_3)_6]$ and $[(C_6H_5)_4As]_2[Pb(N_3)_6]$[4] are soluble and thermally stable in some organic solvents. The electronic absorption spectrum of $[Sn(N_3)_6]^{2-}$ in acetonitrile displays long-wavelength bands (Figure 1) at λ_{max} = 264 nm (ϵ = 4700) and λ_{max} = 236 nm (ϵ = 14 000). Corresponding absorption bands of $[Pb(N_3)_6]^{2-}$ (Figure 1) occur at 390 nm (ϵ = 7420; shoulder) and 318 nm (ϵ = 19500).[4,5]

Upon light absorption, $[Pb(N_3)_6]^{2-}$ (Figure 2) and $[Sn(N_3)_6]^{2-}$ dissolved in acetonitrile underwent an efficient decomposition.

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(2) (a) Cox, A. *Photochemistry* **1984**, *15*, 188. (b) Cox, A. *Ibid.* **1983**, *14*, 179. (c) Kelly, J. M.; Long, C. *Ibid.* **1983**, *13*, 211.

(3) The redox photochemistry of tin compounds is used for electroless metal decomposition; see, e.g.: Paunovic, M. *J. Electrochem. Soc.* **1980**, 127, 441C.

(4) Beck, W.; Fehlhammer, W. P.; Pollmann, P.; Schuierer, E.; Feldl, K. *Chem. Ber.* **1967**, *100*, 2335.

(5) The structured band between 250 and 280 nm is due to the absorption of $[(C_6H_5)_4As]^+$.

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