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Conformation Preferences of 1,2-Dichlorotetranitroethane

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The dipole moments of 1,2-dichlorotetranitroethane in carbon tetrachloride and benzene show that the compound favors the *gauche* conformer in solution-state. Experimentally derived values of the energy difference between the *gauche* and *trans* conformers and their population quotient are compared with values estimated by ab initio calculations. The agreement between experiment and theory is found to be excellent.

Earlier studies on *vic*- dihalo, dicyano and dinitro alkanes containing phenyl or alkyl substituents have shown contrasting results, with the dihalo and dicyano series of compounds existing mainly in the less sterically hindered *trans* form and the dinitro compounds favoring the *gauche* conformation.[1–3] The stability of the *gauche* rotamer in the dinitro and tetranitro[4] compounds has been attributed to the *gauche* effect,[5] whereby the favored structure would have the maximum number of *gauche* interactions between adjacent electron pairs and/or polar bonds. Since dihalogenated-tetranitroethanes have so far not been studied with respect to rotational isomerism, even though they offer an interesting subject for examining the influence of the *gauche* effect on the conformation of the dihalogenated moiety, we therefore decided to undertake a systematic study of this class of compounds. We now report our findings on 1,2-dichlorotetranitroethane (**1**) based on dipole moment determination and ab initio calculations.

Dipole moments of **1** (Table 1) were determined using the method of LeFevre and Vines.[6] The results show that the dipole moment values decrease with increasing temperature in both carbon tetrachloride and benzene solutions, indicating that the *gauche* conformer is more stable than the *trans*, and is higher in population in these solvents. Application of the Lennard–Jones–Pike method of analysis[7] yields a ΔG ($= \Delta G_{gauche} - \Delta G_{trans}$) value of -0.27 kJ mol^{-1} and -0.75 kJ mol^{-1}, with the dipole moment of the *gauche* conformer (μ_g) being 10.69×10^{-30} Cm and 10.54×10^{-30} Cm in carbon tetrachloride and benzene respectively. The corresponding proportion of *gauche* rotamer at 25 °C is 69% and 73% in carbon tetrachloride and benzene respectively.

These results contrast with those for 1,2-dichlorotetracyanoethane (although both the cyano and nitro groups are equally polar with group moments of ca. 13.0×10^{-30} Cm)[8] which favor the *trans* conformation in carbon tetrachloride solution. This difference in conformational behavior may be attributed to the different shapes of the cyano and nitro moieties; the cyano group is cylindrical, whilst the nitro group (being angular) allows the electron pairs to be arranged in closer proximity to one another, thus enhancing the attractive *gauche* interaction.[5] In **1**, the *gauche* configuration contains three *gauche* interactions, whilst the *trans* form has only two such interactions. This attractive *gauche* interaction clearly overrides the steric repulsion between the halogen atoms such that the two chlorine atoms are placed at *gauche* positions to one another. Interestingly, 2,2,3,3-tetranitrobutane also favors the *gauche* conformation in solid-state and in benzene solution, but exists predominantly in the *trans* form in carbon tetrachloride solution.[4]

In the gas phase, the *gauche* form is again preferred (Table 2). The calculated dipole moment is quite small (10.03×10^{-30} Cm) and is in good agreement with the values determined experimentally. With such a small dipole moment, solvent is expected to have minimal effect on the structure, and this is in fact what is observed experimentally. The most stable *trans* form was found to possess a C_2 symmetry (Fig. 1) with the optimized torsion angle (ϕ) and dipole moment being 160.0° and 2.19×10^{-30} Cm, respectively.

The enthalpy difference (ΔH_{298}) between the two forms at 298 K is estimated to be -3.7 kJ mol^{-1} in the gas phase, in favor of the *gauche* rotamer. The entropic factor favors the *trans* form so that the ΔG_{298} is in fact quite small in the gas phase (-0.8 kJ mol^{-1}). From the ΔG_{298} value, **1** is estimated to exist in 58% *gauche* form in the gas phase.

As the *gauche* form has a larger permanent molecular dipole moment, a more polar solvent would favor this rotamer. Our

Table 1. Molar Polarization and Dipole Moments at Infinite Dilution of **1**

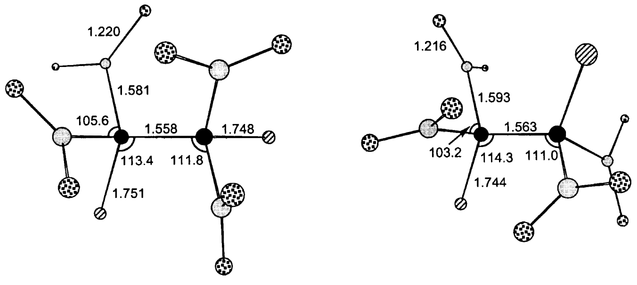
T/°C	Solvent	Conc. range ($10^5 w_2$)	$\alpha\varepsilon_1$	β	P_2/cm^3	$\mu^{a)}/10^{30}$ Cm
7	CCl_4	150–265	5.38	−0.040	206.9	9.08 ± 0.03
25	CCl_4	180–235	4.50	−0.028	191.0	8.88 ± 0.03
45	CCl_4	165–270	4.03	−0.011	176.1	8.70 ± 0.03
7	Benzene	155–270	3.37	0.581	208.9	9.13 ± 0.04
25	Benzene	140–290	3.01	0.612	194.8	9.01 ± 0.03
45	Benzene	130–350	2.38	0.433	184.4	8.94 ± 0.02

a) $P_D = 1.05R_D$; R_D(calc) = 43.72

Table 2. Thermodynamic Quantities Governing the *Gauche*/*Trans* Equilibrium of **1**

	Gas phase	CCl_4	H_2O
$\Delta H_0{}^{a)}$/kJ mol^{-1}	-2.3	-3.2	-4.3
$\Delta H_{298}{}^{a)}$/kJ mol^{-1}	-3.7	-4.7	-5.8
$\Delta G_{298}{}^{b)}$/kJ mol^{-1}	-0.8	-1.7	-2.8
% *gauche* at 298 K	58%	67%	76%
$\mu_g{}^{c)}/10^{-30}$ Cm	10.03	10.83	11.99
$\phi^{\,c)}/°$	59.2	59.0	58.8

a) Enthalpy difference, $\Delta H = H_{gauche} - H_{trans}$. b) Gibbs free energy difference, $\Delta G = \Delta G_{gauche} - \Delta G_{\mathrm{trans}}$. c) Calculated at the B3-LYP/6-31G(d) level in the gas phase, and B3-LYP/6-31G(d)-Onsager level in CCl_4 and H_2O.



1 (*gauche*, C_1) **1** (*trans*, C_2)

Fig. 1. Optimized geometry of the *gauche* and *trans* form of **1** at the B3-LYP/6-31G(d) level.

calculated percentage *gauche* rotamer in carbon tetrachloride is 67%, which is in very good agreement with that determined experimentally in this solvent. Such good agreement lends supports to the theoretical model employed in this study. In a more polar solvent like water, the *gauche* population is estimated to be 76%.

Experimental

Preparation of 1. **1** was prepared according to the method of Borgardt, Seeler, and Nobel.[9] A yellow suspension of dipotassium tetranitroethane (1.60 g, 5.6 mmol) in anhydrous ether was cooled to −10 °C in a dry ice-acetone bath. Dried chlorine gas was slowly introduced whilst maintaining the temperature of the reaction mixture at −10 °C. The white precipitate formed was filtered from the solution. The filtrate was concentrated to give a light yellow solid residue, which upon recrystallisation with 1:1 hexane–ethyl acetate gave **1** as a white solid (1.32 g, 85%), mp 104 °C. Anal. Calcd for $C_2Cl_2N_4O_8$: C, 8.61; N, 20.08; Cl, 25.42%; M, 279. Found: C, 8.59; N, 19.94; Cl, 25.22%; M^+, 279.

Dipole Moment Determination. Dielectric constants were determined with a heterodyne-beat meter and densities and refractive indices were determined by standard procedures.[10] The physical constants required in the dielectric measurements have been given previously.[11]

Calculations. Theoretical geometries, zero-point energies and dipole moments in the gas phase were obtained at the B3-LYP/6-31G(d) level of theory using the GAUSSIAN98 package of program.[12] The initial geometry of the *gauche* form of **1** was obtained from the crystal structure of 2,2,3,3-tetranitrobutane[4] by replacing the terminal methyl groups with chlorine atoms. The *trans* form of **1** was obtained from the *gauche* form by setting the initial torsion angle Cl–C–C–Cl (ϕ) to 180.0° and allowing the structure to optimize fully. Solvent effect on the structures was estimated by the Onsager model[12] at the B3-LYP/6-31G(d) level using a dielectric constant of 2.2 for carbon tetrachloride and 80.1 for water, with a cavity radius of 4.65 Å. Relative energies were computed at the B3-LYP/6-311+G(d) level in the gas phase and B3-LYP/6-311+G(d) level with the polarized continuum model (PCM) of Tomasi in solution.[12] Standard thermodynamic relations were applied to obtain ΔH_{298} and ΔG_{298}.

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