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Consistent Force Field Calculations on the Geometry of Triethylamine

Short Communication

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Consistent force field calculations on the geometry of triethylamine are presented and compared with experimental results. Triethylamine seems to exist mainly in a conformation with all ethyl groups *cis* to the lone pair electrons at the nitrogen atom.

(Keywords: Consistent Force Field Calculations, Triethylamine)

Kraftfeldberechnungen der Geometrie von Triethylamin (Kurze Mitteilung)

Consistent Force Field Rechnungen der Geometrie von Triethylamin werden mit experimentellen Ergebnissen verglichen. Triethylamin existiert dann in der günstigsten Konformation, wenn alle Ethylgruppen *cis* zum einsamen Elektronenpaar des Stickstoffs stehen.

The peculiar properties of phenol—aliphatic amine interactions have been emphasized by several authors[1–7]. The thermodynamic and in particular the kinetic behavior of these systems shows some unexpected characteristics which are not yet completely understood.

The addition of triethylamine (*TEA*) to 2,4-dinitrophenol in chlorobenzene leading to hydrogen bond formation and subsequent proton transfer, has been investigated by chemical relaxations methods[6,7]. For the rate constant of the addition step a value of $k_f = 1.7 \cdot 10^8\,M^{-1}\,s^{-1}$ has been measured, which is below the limit of diffusion-control by a factor of about 50. This difference can be understood as an additional activation process due to conformational change or to solvation phenomena. The results of kinetic measurements of the addition of various tertiary aliphatic amines to 2,4-dinitro-phenol are given in Table 1. The

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Table 1. *Rate constants for the addition of 2,4-dinitro-phenol to various bases in chlorobenzene*[6, 7]

Base	k_f (M^{-1} s^{-1})	k_b (s^{-1})
quinuclidine	2.0 (± 0.3) · 10^9	1.7 (± 0.3) · 10^4
triethylamine	1.7 (± 0.8) · 10^9	7.2 (± 0.3) · 10^4
tri-*n*-propylamin	5.1 (± 0.3) · 10^8	1.0 (± 0.05) · 10^5
tri-*n*-butylamine	3.0 (± 0.3) · 10^8	9.0 (± 1.0) · 10^4
tri-*n*-amylamine	3.3 (± 0.2) · 10^8	5.8 (± 0.3) · 10^4
tri-*n*-octylamine	2.4 (± 0.4) · 10^8	5.1 (± 0.8) · 10^4

Table 2. *Conformations of TEA based on force field calculations; A all methyl groups cis to the lone pair electrons; B two methyl groups cis; C one methyl group cis; D all methyl groups trans; energies in kJ mol*$^{-1}$

	A	B	C	D
Total energy	—8720.50	—8714.23	—8714.44	—8714.01
Bond contribution	—8692.14	—8692.31	—8692.38	—8692.31
Non-bond contribution	22.72	25.75	24.98	20.01
Theta-contribution	32.80	31.00	30.21	30.55
Phi-contribution	83.89	78.70	77.24	72.76
ΔE		—6.27	—6.06	—6.49
ΔH_{exp}*		—14.2		

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* H_{exp} was evaluated from an analysis of the observed relaxation process which is associated with the equilibrium between rotational isomers (mean value).

addition of quinuclidine to 2,4-dinitro-phenol is not sterically hindered since the carbon chains are tied back and cannot interfere with the reaction center. Longer aliphatic residues decrease the rate constant k_f drastically. The difference in rate constants k_f between quinuclidine and *TEA* is not significant under the assumption of an increase of activation due to steric repulsion (the dynamic repulsion in the addition complex is mainly reflected in the dissociation constant). Less polar solvents increase the rate constant of the addition step (2,4,6-trichloro-phenol and *TEA* in cyclohexane[8]: $k_f = 5.3 \cdot 10^9 M^{-1}$ s^{-1}, in benzene[9]: $k_f = 2.1 \cdot 10^9 M^{-1}$ s^{-1}) and the values of the rate constants are only a factor of 2 and 5 respectively, below the diffusion limit. However, in cyclohexane a "negative" activation energy was observed formally, as an indication for a more complex mechanism of the addition reaction.

In an attempt to explain these surprising experimental findings, we have performed consistent force field calculations on the geometry of *TEA*. The steric consequence of intramolecular nonbonded interactions

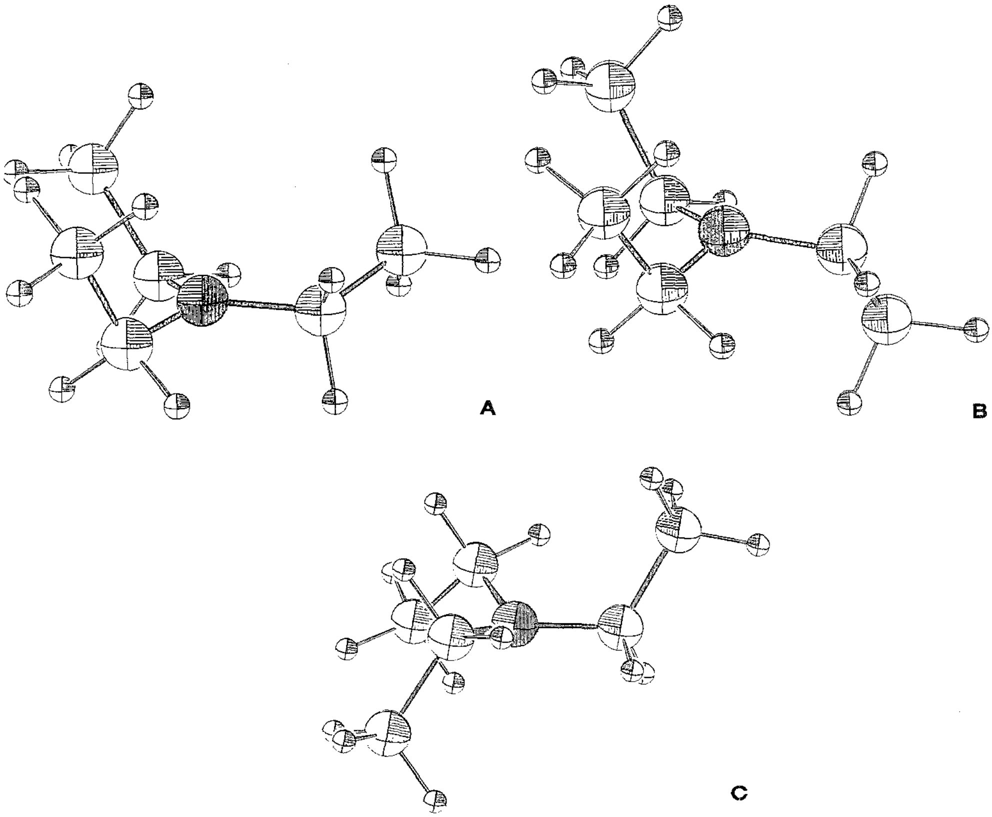

Fig. 1. Conformations of *TEA*; *A* represents the most stable conformation of *TEA*, *B* and *C* have energies of —6.27 and —6.06 kJ mol^{-1} above the ground state conformation

are reflected in a static geometry which should be similar to the situation encountered in an inert solvent like cyclohexane. For the calculations we used a revised version of a computer program by *Warshel* and *Lewitt* with the parameters given by the authors. Additionally, a parameter for the amine nitrogen has been determined by fitting to experimental values. Table 2 shows the energy terms of the most stable conformation of *TEA* together with that of some rotational isomers of somewhat higher energy. In Fig. 1 the conformation of the energy minimum and two of the geometries of higher energy are represented. Our calculations reveal that the conformation with all ethyl groups *cis* to the lone pair electrons of the nitrogen atom (conf. A) is 6.1 kJ mol^{-1} less strained than either conformation B or C, with one or two methyl groups *trans* to the lone pair electrons. *TEA* seems to exist mainly as a twisted "crown". The conformations with one or more methyl groups distorted into an other direction do not contribute for more than 30% of the total population at room temperature. Conformers with all ethyl groups twisted are very unfavorable.

Ultrasonic relaxation experiments carried out on pure *TEA* and on *TEA* dissolved in aprotic media[10,11] show a single relaxation process which is considered to be connected with an equilibrium between rotational isomers of different energies. Such experiments have been conducted over a wide temperature range, the resulting thermodynamic parameters are also given in Table 2. These enthalpy values are somewhat higher than the calculated energy differences.

Calculations on protonated *TEA* do not show any change in the sequence of the energy levels for the different geometries—the conformations of protonated and neutral *TEA* are the same with regard to the position of the methyl groups. Therefore we conclude that the reaction center is not too crowded for addition of molecules building up a hydrogen bond, as long as the attacking group is not too bulky, such as in phenols with large substituents in the ortho position.

In the case of tri-*n*-propylamine the energy differences between various rotational isomers are relative low—a fact which has also been observed in ultrasonic absorption measurements on the higher homologue ($\Delta H = 3.6\,\mathrm{kJ\,mol^{-1}}$ for tributylamine[12])—the freedom of movement of the alkyl side chains is high; the larger alkyl groups interfere easily with addition on the reaction center.

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