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MOLECULAR STRUCTURE AND ASSOCIATION OF DIPHENYLGUANIDINE IN SOLUTION

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An experimental and theoretical study of the structure and aggregation of diphenylguanidine (DPhG) in non-polar and low-polarity solvents (CCl_4, C_6H_6, C_2HCl_3 and $CHCl_3$) was performed. Dipole moments, IR spectra and average molecular weight measurements as a function of concentration demonstrate that DPhG is strongly associated in the solvents studied. The dimerization constant in CCl_4 is 192 ± 7 dm^3 mol^{-1}. Experimental results and a theoretical discussion on the basis of MNDO–PM3 and –AM1 methods show that in low-polarity solvents DPhG exists in the form of an asymmetric tautomer, the same as was found in the solid-state structure.

INTRODUCTION

The structure, thermodynamic and spectroscopic characteristics of hydrogen-bonded complexes, formed by molecules possessing a few functional atoms or atomic groups able to enter into intermolecular interaction, are defined by the peculiarities of their electronic and molecular structures. It has been demonstrated that compounds such as pyrazoles, triazenes and amidines[1–3] form open associates with the linear H-bond and also cyclic structures with several H-bonds, where the NH group plays a role of a proton donor and the basic nitrogen atom is a proton acceptor.

In this work, we carried out a study on the association of *N,N'*-diphenylguanidine (DPhG), a molecule which can participate in resonance leading to so-called Y—aromacity,[4] causing a substantial delocalization of three C—N bonds in the guanidine moiety, which becomes especially effective in monocations (owing to this the pK_a of guanidine is 13·6;[5] the pK_a of DPhG is 10·12).[6] Their NH groups are potential proton donors. The C=NH group has a high proton-acceptor ability. For these reasons, DPhG molecules seem to be able to form different types of H-bonded associates. The situation becomes more complex when one considers the possible tautomeric equilibrium of the DPhG molecule.

The study of the structure of DPhG molecules and other guanidine derivatives, their intermolecular interaction and the parameters of their H-bonded complexes seems to be important also from the practical point of view.[3] These compounds, very effective in the formation of hydrogen bond nets, can be used for peptide denaturation in biochemical studies of secondary and tertiary structures,[7] for the production of cellulose[8] and as effective agents in the extraction of metals from acidic media.[9] The IR absorption spectra of solid DPhG have been obtained[10,11] and also its UV spectra.[11,12] From the Raman spectra of polycrystalline DPhG and its complexes with carboxylic acids,[13,14] the conclusion was drawn that both linear and cyclic H-bonded structures exist.

Structural analysis of crystalline DPhG using the x-ray diffraction[15] showed that of two possible tautomeric forms (Scheme 1) the less symmetrical form *II* occurs in the crystal, where the central carbon atom and three nitrogen atoms form a common plane. Experimental data on the tautomeric structures of DPhG and its association in solution are lacking; only the IR spectra of DPhG and triphenylguanidine in CCl_4 solution have been obtained and analysed.[14]

In order to determine the character of the association and the structure of the complexes formed in solution,

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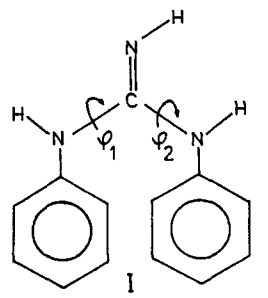

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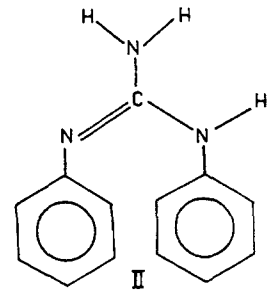


II

Scheme 1

we have studied the IR absorption spectra, the molecular weight and dipole moments of DPhG in the low-polarity solvents CCl_4, C_6H_6, $CHCl_3$, CH_2Cl_2 and C_2HCl_3. Quantum chemical calculations for the DPhG molecule were also performed. The potential energy (ΔH_f°) surface was determined by the semi-empirical MNDO–AM1 and –PM3 methods. For a comparatively large molecule such as DPhG, more advanced *ab initio* techniques could not be applied in a such calculations. The strong π-electronic coupling in the molecule makes the use of molecular mechanics methods less advisable.

EXPERIMENTAL

Commercial *N,N'*-diphenylguanidine (chemically pure grade) was purified by multiple recrystallization from benzene. The solvents used were subjected to fractional distillation and dried over KOH. IR absorption spectra of solutions were recorded by Fourier transform spectrophotometry (Nicolet 205) and UR-20 Carl Zeiss, Jena, Germany at the room temperature with a resolution of 2 cm^{-1} in cells with CaF_2 or quartz windows; the optical path was varied from 0·55 to 50 mm. The solution concentration was varied from 5×10^{-4} to 0·1 mol dm^{-3}. Dipole moments (μ) of DPhG in solution were determined by the heterodyne beat method at 2 MHz on a DMO1 (WTW) dipolemeter. Calculations were performed by the Onsagel method (in CCl_4, C_6H_6, $CHCl_3$ and C_2HCl_3) or the Hedestrand method (only for CCl_4 and C_6H_6).[16] The μ values obtained by these two methods coincided at the limit of experimental error, ±0·1 D. Solutions of different concentration (from 1×10^{-3} to 0·1 mol dm^{-3}) were used. Other experimental details have been described previously.[17]

The average molecular weights, M, in DPhG solution were determined by using an Osmomat 070 apparatus (Gonotec) in the temperature range 35–55 °C.

Semi-empirical calculations on the DPhG molecule were performed by the MNDO–PM3 and –AM1 methods at the 'precision' level (MOPAC 5·0 version)[18] and by the version with SCRF implemented.[19]

RESULTS AND DISCUSSION

Dipole moments

Figure 1 illustrates the dependences of the dipole moment of DPhG on its concentration in different solvents. The standard deviation of a single measurement of μ is 0·05.

An increase in the solution concentration causes a decrease in μ^2 in all cases, but in a different manner. It is much steeper in CCl_4 and C_2HCl_3 than in C_6H_6 and $CHCl_3$. An increase in the polarity of the solvent (electric permittivities are 2·2, 2·3, 3·4 and 4·8 for CCl_4, C_6H_6, C_2HCl_3 and $CHCl_3$ respectively) results in a weakening of the dependence of μ on concentration. Despite the low polarity of benzene, a typical enhanced 'activity' of this solvent is observed. The type of dependences observed suggest the formation of low-polarity forms of associates in solution.

Values of μ for the monomeric DPhG molecule in different solvents were estimated by extrapolation to zero concentration and were 3·72 D in CCl_4, 3·44 D in C_6H_6, 3·88 D in C_2HCl_3 and 3·9 D in $CHCl_3$. The dipole moment of the DPhG molecule has been measured[20] in benzene at 30 °C and the value of 3·14 D is in agreement with the results of our work, considering

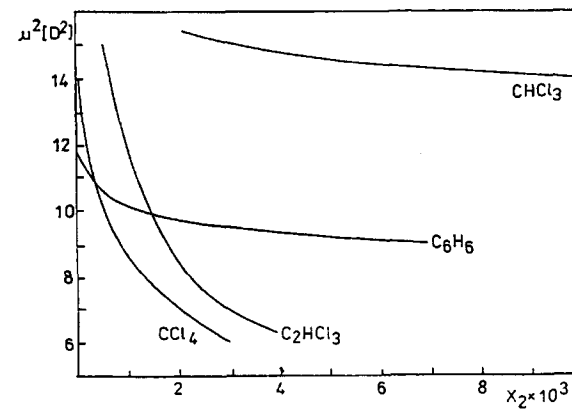


Figure 1. Concentration dependence of DPhG dipole moments at 25°C. x_2 = Molar fraction of solute

the concentration dependence of the measured, average dipole moment.

The results obtained in CCl_4 solution were analysed more detail using a dimerization constant of 192 ± 7 dm^3 mol^{-1} (see IR spectra section) on the basis of the equation:

$$y = \mu_{eff.}^2(x_M + 2x_D) = \mu_D^2 + x_M(\mu_M^2 - \mu_D) \quad (1)$$

Details of this method and literature citations are given in Ref. 17.

The experimental results fit the linear equation $y = 5{\cdot}487\ (\pm 0{\cdot}636) + 10{\cdot}488\ (\pm 1{\cdot}152)x_M$ with a correlation coefficient $r = 0{\cdot}9767$ for $n = 6$, giving $\mu_M = 3{\cdot}99 \pm 0{\cdot}23$ D and $\mu_D = 2{\cdot}34 \pm 0{\cdot}14$ D. This more precise estimated value of μ_M is higher than that obtained by direct extrapolation of $\mu_{eff.}^2$ to zero concentration (equal to 3·72 D) by 0·27 D. One can consider the precision of μ_M determination, in this case, to be better than ±0·3 D. The original values and details of the fitting procedure are given in deposited material.

Such an analysis was not possible in other solvents, because K_{eq} of association cannot be determined owing to solvent absorption. As has been shown,[21,22] the simultaneous determination of the association constants and dipole moments of monomers and dimers is much less reliable.

Average molecular weight

The average molecular weights of DPhG were determined in different solvents at 35, 45 and 55 °C within the range of concentrations which approximately coincided with the concentrations used in the measurements of dipole moments. An increase of molecular weight with increase in solution concentration was recorded for all solvents; some dependences at 45 °C are presented in Figure 2.

It is characteristic that in all cases the M values do not reach twice the molecular weight of the monomer

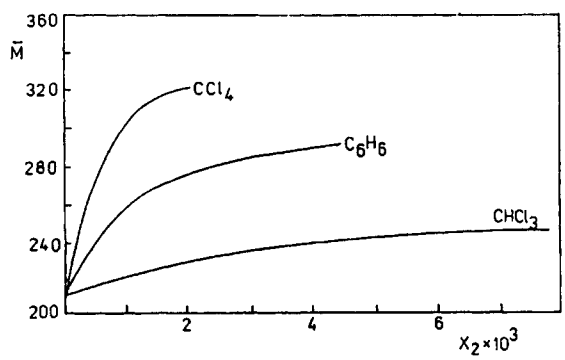


Figure 2. Dependence of M values on DPhG concentration in different solvents at 45°C. x_2 = Molar fraction of DPhG

(M_{mon}). The maximum value of M/M_{mon} found in our determinations was 1·75 (in CCl_4 at 55 °C). This means that it is unlikely that associates higher than dimers can participate in the equilibrium with monomers in the applied ranges of temperatures and concentrations. A similar association of DPhG molecules was reported by Hunter and Marriott,[23] where molecular weights of DPhG were determined in naphthalene solution by means of the cryoscopic measurements. At all temperatures studied, the degree of association decreases with increase in the solvent polarity (see Figures 2).

Association equilibria

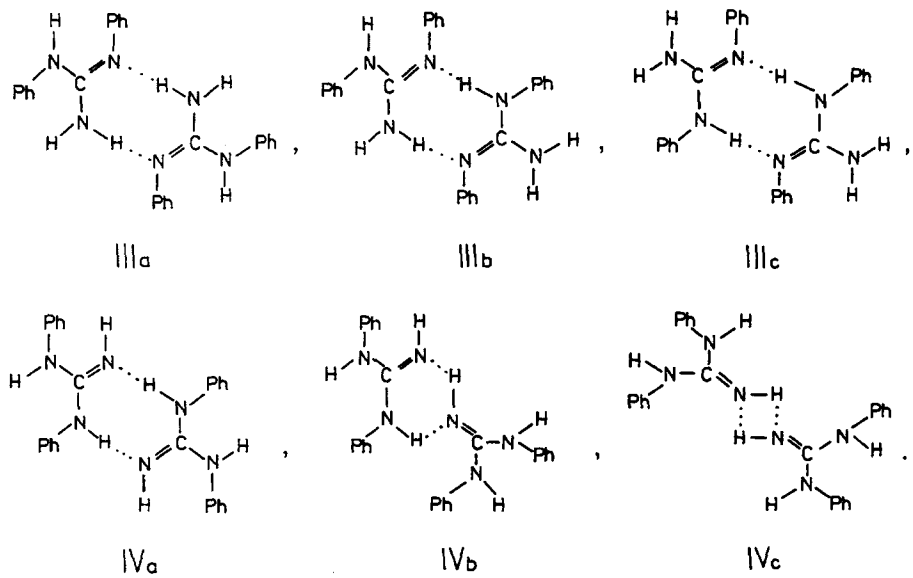
The results obtained and the determined values of the dipole moments indicate the preferred formation of non-polar, cyclic DPhG associates in the solvents studied. For possible DPhG tautomers **I** and **II**, the structures of the cyclic dimers shown in Scheme 2 can be suggested. For tautomer **II**, preferred in the literature (refs 3, p. 502, and 15), either two NH_2 amino groups (**IIIa**) or NH_2 and NHPh (**IIIb**) or only NHPh groups (*IIIc*) can act as protono donors; for the symmetrical tautomer **I** it is possible to propose eight—(**IVa**), six—(**IVb**) and four-membered (**IVc**) cyclic dimers.

The strong basicity of the DPhG molecule in analogy with guanidine is attributed to the C=N—H centre. The proton-donor ability of this group is almost zero.[3] For this reason, and because of non-linearity of hydrogen bridges, the possibility of the formation of structures **IVb** and **IVc** must be considered very small. The existence of free, non-bonded NH groups in the proposed structures suggests the possibility of joining additional DPhG molecules to the cyclic dimer, with the formation of trimers or higher associates. The molecular weight and dipole moment measurements (see above) do not support such a suggestion, at least for the concentration range studied. The study of more concentrated solutions is impossible because of the low solubility of DPhG in low-polarity solvents.

Applying the association model $A + A \rightleftharpoons (A)_2$, we estimated the values of the association constants:

$$K_{eq} = C_{ass}/C_{mon}^2 \quad (2)$$

from the data from the molecular weights measurements. The values of K_{eq} obtained at 45 °C are 180 ± 50 dm^3 mol^{-1} in CCl_4, 38 ± 7 dm^3 mol^{-1} in C_6H_6 and 6 ± 2 dm^3 mol^{-1} in $CHCl_3$. At 55 °C the corresponding values are 130 ± 30 dm^3 mol^{-1} in CCl_4 and 30 ± 15 dm^3 mol^{-1} in C_6H_6. The high experimental uncertainty of K_{eq} determination makes it difficult to calculate the dimerization energy. The observed decrease in the amount of complex molecules with increase in solvent polarity supports the assumption of the cyclic structure of DPhG, dimers in non-polar solution.[3]



Scheme 2

IR spectra

Important additional information was obtained from the IR absorption spectra of DPhG solutions (Figures 3 and 4) in CCl_4, $CHCl_3$ and CD_2Cl_2 (all measurements were made at room temperature).

In all the spectra, in the stretching vibration νNH region two high-intensity bands (3505 and 3404 cm^{-1} in CCl_4) are observed in addition to one wide structured band increasing in intensity with increase in DPhG concentration. This absorption lies in the range 3300–2700 cm^{-1} with a centre of gravity at 2950–3000 cm^{-1} (for different solvents), overlapping the νCH vibration bands. A low-frequency component of the intense doublet has a structure which is clearly resolved for solutions in CCl_4 (3445 and 3430 cm^{-1})

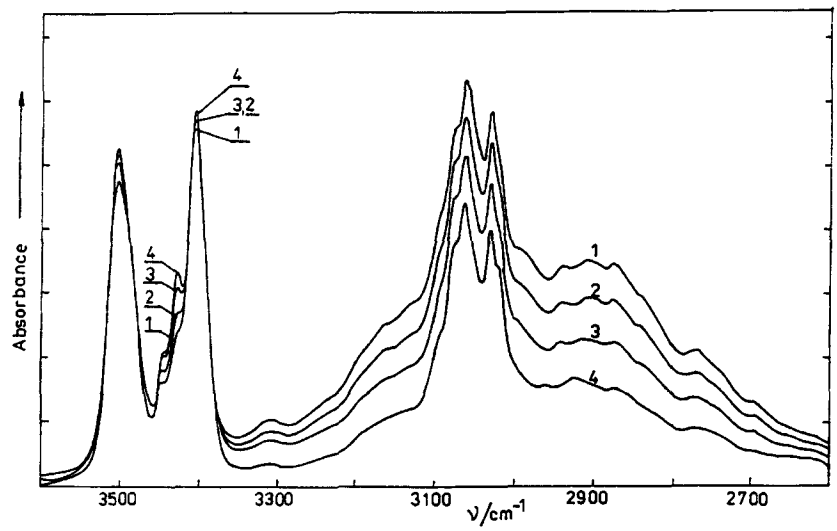


Figure 3. IR absorption spectra of DPhG in CCl_4 solution at concentrations of (1) $1{\cdot}25 \times 10^{-2}$, (2) $6{\cdot}25 \times 10^{-3}$, (3) 12×10^{-3} and (4) $1{\cdot}25 \times 10^{-3}$ (cl = constant)

and less marked for more polar solvents, where only a weak high—frequency shoulder on the 3400 cm^{-1} band can be recorded. The bands in the 3400–3500 cm^{-1} region could be definitely attributed to the νNH absorption of free functional groups and that at 3000 cm^{-1} to associated NH groups.

The observed IR absorption spectra can be explained on the assumption that structure II of DPhG predominates in solution (as in the crystal phase[3,15]). The bands at 3500 and 3400 cm^{-1} can be assigned to ν_{as}NH and ν_sNH vibrations of the NH_2 group.[10,14] Unlike the absorption in the region of 3000 cm^{-1}, the intensity of these bands depends very weakly (Figure 3) on the DPhG concentration. The high-frequency components of the 3400 cm^{-1} band become markedly weaker with increase in concentration, and therefore they could be assigned to the νNH vibration of NHPh free groups [in the crystal phase this νNH absorption is observed at 3450 cm^{-1} (Ref. 14)]. The existence of two components in non-polar solvents can be explained by a small participation of tautomer I in the equilibrium.

The equilibrium in solution cannot be shifted completely to the dimers or monomers under our experimental conditions and for this reason it was not possible to determine the molar absorptivities of the free or associated νNH bands or to calculate the equilibrium constant of association (K_{eq}). An additional complication would be the existence of non-bonded NH groups in the DPhG cyclic dimmer (Scheme 2). For these reasons, we applied a less precise method, based on the assumption that only dimerization proceeds in solution. Then,

$$C_0 = 2C_D + C_M \quad (3)$$

where C_0, C_D and C_M are the formal concentrations of the solute, dimer and monomer, respectively. Simultaneous solution of equations (2) and (3) allows the calculation of C_D for an assumed K_{eq} value. In the spectral region where only dimer absorption is observed,

$$E/l = \varepsilon_D C_D \quad (4)$$

where E is the experimental absorptivity of solution, l the cell length and ε_D the molar absorptivity of the dimer. In searching for the best K^{eq} value, equation (4) was fitted for a set of experimental E values obtained for different C_0 (eight values in our case), obtaining the smallest standard deviation from the straight-line equation, by adjusting a trial K_{eq} value. By processing the absorptivity values at three different wavenumbers (2928·8, 2906·7 and 2886·8 cm^{-1}), an average value of $K_{eq} = 192 \pm 7$ $dm^3\,mol^{-1}$ was estimated in CCl_4 solutions (at 25 °C), coinciding with the results of molecular weight measurements. The uncertainty range of K_{eq} determination appeared to be much less than when using the average molecular weight method. This confirms our observations from the association of 2-oxoindolinone studies.[17] Also, the value of K_{eq} for DPhG appears to be similar to the equilibrium constants estimated for cyclic dimerization of 2-oxoindolinones.

The comparatively large shift of νNH observed for DPhG in CCl_4 solutions is similar to that observed for diphenylformamidine,[1,2] which has a very similar structure to DPhG. A structured band with $\Delta\nu$NH = 500 cm^{-1} was recorded, which was assigned to the νNH band of cyclic dimers. The K_{eq} value of 20 ± 4 $dm^3\,mol^{-1}$ obtained for diphenylformamidine in $CDCl_3$ at 25 °C[2] is similar to that obtained for DPhG from molecular weight measurements in this work.

A wide structured νNH band has also been observed for substituted pyrazoles.[3,24] The shape of the band of associated molecules appears to be sensitive to deuteration, but it does not depend on variations of concentration and temperature. Thus, the νNH band structure of bonded NH groups at 3000 cm^{-1} can be interpreted in terms of Fermi resonance rather than the formation of complexes with different structures and compositions.

Very characteristic changes were observed in the region of νC=N absorption (see Figure 4), which can be an additional argument in favour of the cyclic dimerization of DPhG. When the concentration of DPhG increases, a new low-frequency component of ν_{mon}C=N (1660 cm^{-1} in $CHCl_3$) appears, shifted by 20 cm^{-1}, and its intensity increases with increase in concentration. In CD_2Cl_2, the low-frequency band, which we attribute to the ν_{ass}C=N absorption of the hydrogen bonds, was not resolved; it appears as a shoulder on a strong νC=N band. Such changes in the νC=N band, taking place simultaneously with the appearance of the 'bonded' νNH band, show that the both proton-donor NH groups and the basic centre

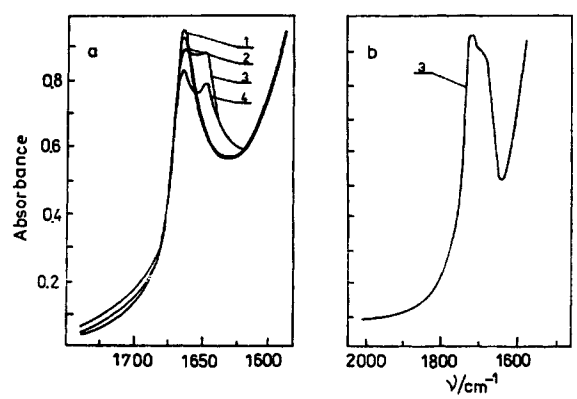


Figure 4. IR spectra of DPhG solutions in the νC=N absorption region in (a) $CHCl_3$ and (b) CD_2Cl_2 at concentrations of (1) 0·025, (2) 0·05, (3) 0·075 and (4) 0·1 mol dm^{-3}

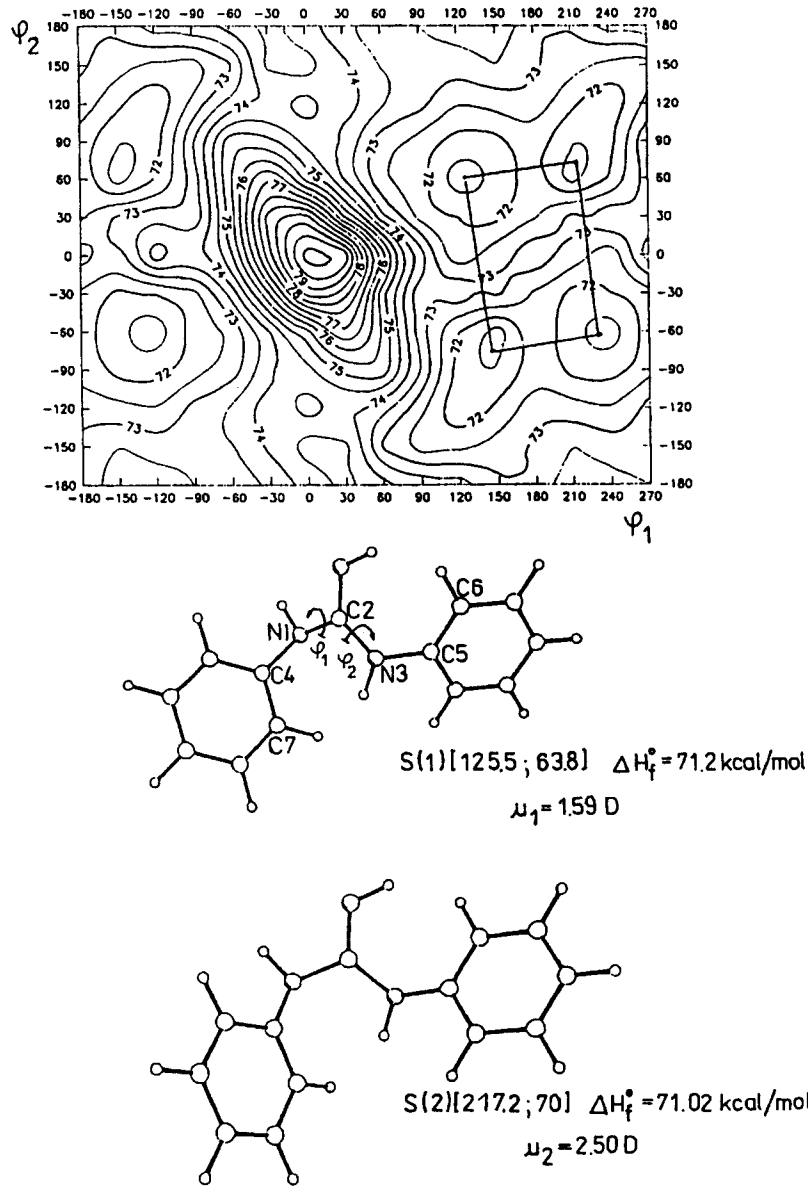


Figure 5. Potential energy (ΔH_f°; in kcal mol^{-1}) surface calculated by the MNDO–PM3 method for symmetric tautomer I of DPhG. The structures represent two independent conformers of the lowest energy

C═N participate in the formation of hydrogen-bonded DPhG associates.

It is difficult to select definitely one certain model of association. Because the PhNH group is considered to be a stronger proton donor[25] than the HNH group, structure **IIIc** is more preferable than **IIIb** and **IIIa** (for the 'asymmetric' DPhG form **II**). Such an assumption explains also the very weak decrease in the intensity of symmetric and antisymmetric vibrations of the NH_2 group with increase in concentration.

Semi-empirical calculations

The arguments in favour of the tautomer **I** or **II** for the DPhG molecule can be obtained from calculations of electronic charge distribution and the potential energy surfaces of the DPhG molecule.

Both tautomers possesses a few degrees of freedom for rotation. To answer the question about the relative stability of the two forms, complete optimization of the structure has to be performed. It requires extensive calculations to obtain the potential energy surface (PES) for the two tautomers, and we decided to begin the semi-empirical quantum mechanical calculations with the PM3 procedure, which is known to be better than other semi-empirical methods for description of the hydrogen bond structure.[18]

The results of the calculations for tautomer **I** are shown in Figure 5.

A planar conformation, such as that shown in Scheme 1 (φ_1, $\varphi_2 = 0$; φ_1 is the C4—N1—C2—N3 angle and φ_2 the C5—N3—C2—N1 angle) appears to be the least probable state. Four distinct minima on the potential energy surface are seen at almost the same level of ΔH_f°. Two structures of conformers (the upper ones on the PES in Figure 5) are shown. Two others are related by the symmetry centre located at the point ($\varphi_1 = 180°$, $\varphi_2 = 0°$). Interconversion between these structures is connected with passing one barrier of about 1 kcal mol^{-1} (1 kcal = 4·184 kJ) on the shorter (nearly horizontal) path and the second about 2 kcal mol^{-1} on the longer (nearly vertical) path (as shown in Figure 5). The φ_3 and φ_4 angles, defined as C7—C4—N1—C2 and C6—C5—N3—C2, are, respectively, −73·4° and 62·1° for S(1) and −71·8° and 123·25° for S(2). Further, these parameters are not considered separately. They are optimized without restraint as all the other parameters of the molecule. Separate calculations of the potential for φ_4 rotation for structures S(1) and S(2) (compare deposited material) show relatively free rotation of phenyl rings with barriers of 2 kcal mol^{-1}. Accepting even erroneous conformations at local minima, with respect to φ_4, hardly changes the location of the minima on the surface in Figure 5. The calculated dipole moment changes by less than 0·2 D on this rotation.

The results of the PM3 calculation for tautomer **II** are shown in Figure 6. The different character of the potential energy surface obtained is clearly seen. The rings in this tautomer are not equivalent. Rotation around the C—N (sp^3) bond is almost free relative to the rotation around the C═N bond. There are three regions of low energy characterized by $x = 0$ and ± 1800 (last two states are equivalent for symmetry reasons). The dynamic conformation of the molecule inside such formed energetic valleys can be characterized by a potential energy dependence on y for restricted $x = 0$ or 180°. The most stable structures were found for $y \approx \pm 120°$ at $\Delta H_f^\circ = 67{\cdot}9$ kcal mol^{-1}, for both $x = 0$ and 180°. The activation barrier for rotation around a single C—N bond is 1·8 kcal mol^{-1} for $x = 180°$. For the second planar conformation ($x = 0°$), the barrier for 'y-rotation' (cf. Figure 6) is higher (by 4·4 kcal) owing to increased steric repulsion of the phenyl ring. The global minima of the two independent structures can be characterized as S(1) (−9·6; 125·4) with $\Delta H_f^\circ = 67{\cdot}637$ kcal mol^{-1} and S(2) (188·6; −136·4) with $\Delta H_f^\circ = 67{\cdot}922$ kcal mol^{-1}. Passing between those states requires rotation around the C═N bond, which is connected with the formal cleavage of a double bond. The calculated barrier height is relatively low, however. Its lowest value for $y = \pm 180°$ is 17·6 kcal mol^{-1}. The transfer for $y \approx 0$ is characterized by a higher barrier of 19 kcal mol^{-1} due to steric repulsions. The values of the activation barrier suggest the effective delocalization of π-electrons within the molecule. The thermochemical energy of π interaction in isolated C═N bond is about 45 kcal mol^{-1}.[26] On the other hand, the calculated value of the activation barrier is higher than the value of 12 ± 1 kcal mol^{-1} (Ref. 3, pp. 485–526) obtained by ^{1}H NMR spectroscopy for rotation around C—N bonds in 2-aryl-1,1,3,3-tetramethylguanidinum cation independent of the formal π character of a particular C—N or C═N bond. The C—N and C═N bonds in DPhG in the PM3 approach are localized to a large extent. The potential energy surfaces calculated by the PM3 method for both tautomers suggest that the DPhG molecule can be characterized by conformational freedom and all active groups are accessible for intermolecular interactions. The levels of ΔH_f° for minima of tautomer **II** are deeper than for **I**, 67·9 and 71·7 kcal mol^{-1}, respectively, the difference being 3·3 kcal mol^{-}. Calculations suggest that also in the gas phase and non-polar solvents the asymmetric tautomer **II** predominates, as in the solid state.[15]

The PM3 method describes relatively well the structure of the hydrogen bridge but underestimates the steric repulsion in the system.[27] In order to make the barrier determination more reliable, we repeated the calculations of the potential energy surface with the AM1 procedure. Calculations for tautomer **I** were performed within the φ_1 and φ_2 ranges which cover the region of the minima localization on potential energy surface (cf. Figure 7).

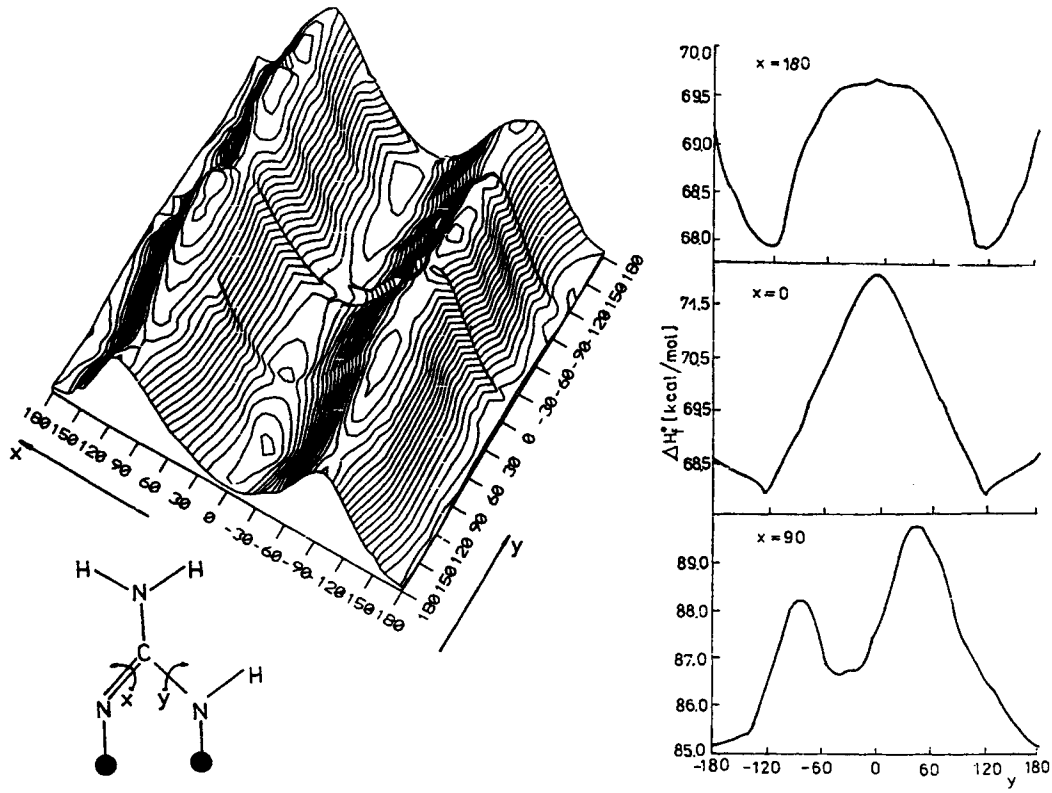


Figure 6. Potential energy surface calculated by the MNDO–PM3 method for the asymmetric tautomer **II**. Potential energy profiles describe the rotation around single and double C—N bonds

The positions of the minima are slightly shifted in comparison with the PM3 results (all independent conformers are characterized in more detail in Table 1). The minima are at different levels of ΔH_f°. There are two ways of interconversion between the states; the barriers for reaching the higher state are 1·9 and 0·76 kcal mol^{-1}, respectively.

The results of calculations of the dynamic structure of tautomer **II** of DPhG with the MNDO–AM1 procedure are shown in the Figure 8. The difference between the lowest energy points for tautomers **I** and *II* estimated by the AM1 procedure is 4·20 kcal mol^{-1}, again in favour of the asymmetric tautomer **II**.

One can try to compare the structural parameters obtained in calculations for the most stable conformers with the crystal structure, despite the reported[15] dependence of the molecular structure on the character of the hydrogen bonds formed by a particular molecule. The molecules in the crystal form chains, not cyclic forms as we have stated in non-polar solutions. These chains form a net of hydrogen bonds of different strength. Considering the conformational flexibility of DPhG molecules, one can compare the bond lengths. In the solid state the C—N bond lengths of the guanidine fragment are 1·350(8), 1·359(7) and 1·288(7) Å, close to lengths calculated by *ab initio* methods for neutral guanidine.[6]. Equilibration of these bond lengths suggests a stronger π-electronic coupling in DPhG than in guanidine. The AM1 calculations gave C—N bonds lengths, averaged for different conformers, of 1·41(2), 1·42(2), 1·327(3) Å, which demonstrates that the applied method underestimates the π-electronic coupling in the central part of a molecule. The C—N bond lengths between phenyl rings and N atoms of the central guanidine moiety are reproduced properly: 1·412 and 1·403 Å compared with 1·14(7) and 1·399(7) Å found in the crystal structure.

The reliability of the structure determination by a particular theoretical method can be verified by comparing of the calculated dipole moments with the experimental values for monomers. For the symmetric tautomer **I** of DPhG, the PM3 method predicts two symmetrically independent minima (Figure 5). Assuming a Boltzmann distribution, one can obtain an average

Table 1 Comparison of calculated and experimental dipole moments in CCl_4 solutions

Tautomer	Method	Permittivity	Minimum location (x, y)	Calculated ΔH_f° (kcal mol^{-1})	Dipole moment (D)	Average dipole moment (D)	Experimental dipole moment (D)
I	PM3	1	S(1) (125·5. 63·8)	71·200	1·59	2·16	—
			S(2) (217·3; 70·0)	71·020	2·50		
		(2·238)	S(1) (127·8; 59·9)	71·005	1·93	2·79	3·99
			S(2) (217·4; 65·0)	70·459	3·07		
II	PM3	1	S(1) (−9·6; 125·4)	67·637	2·19	2·25	—
			S(2) (188·6; −136·4)	67·922	2·35		
		(2·238)	S(1) (−10·2; 126·2)	67·417	2·56	2·62	3·99
			S(2) (188·6; −136·5)	67·665	2·70		
I	AM1	1	S(1) (151·9; 59·3)	88·563	1·76	1·79	—
			S(2) (219·0; 76·2)	89·172	1·89		
		2.238	S(1) (151·9; 59·3)	88.397	1.90	1.98	3.99
			S(2) (218·4; 73·1)	88·968	2·19		
II	AM1	1	S(1) (−4·3; −164·2)	84·364	3·46	2·95	—
			S(2) (172·6; 130·0)	84·381	2·34		
		2·238	S(1) (−3·5; −164·6)	83·520	4·34	3·98	3·99
			S(2) (172·6; 135·1)	84·023	3·00		

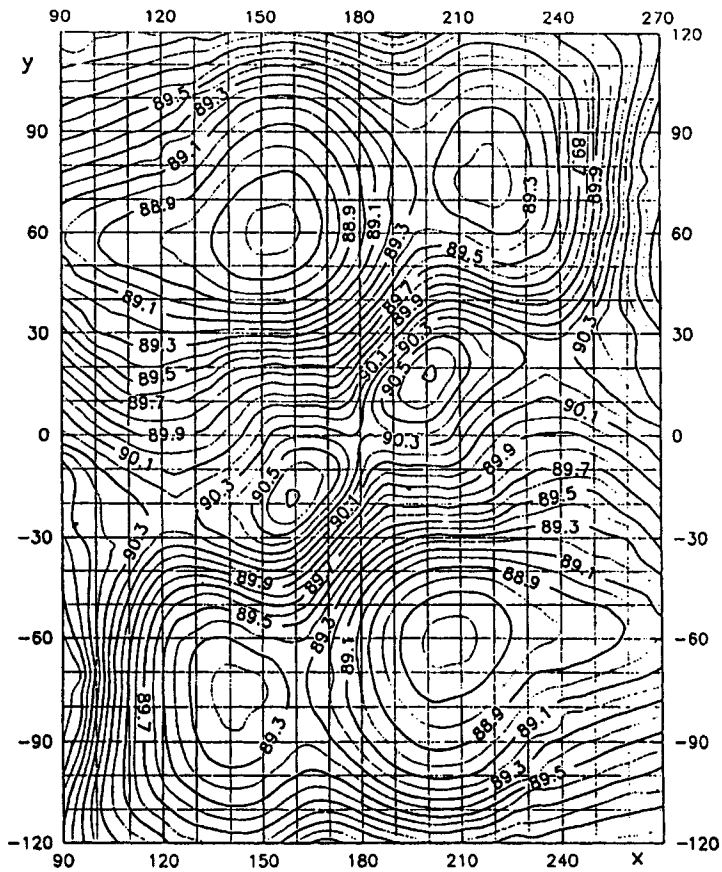


Figure 7. Potential energy surface of symmetric tautomer I calculated by the MNDO–AM1 method

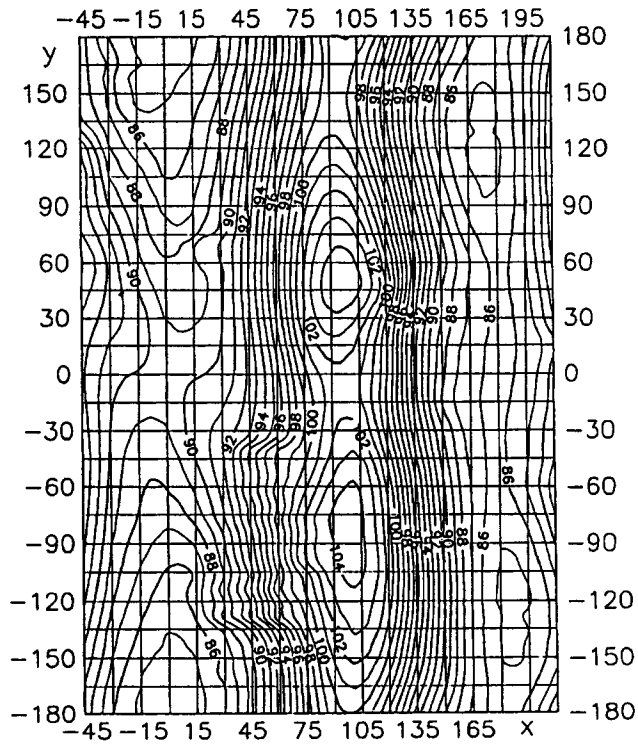


Figure 8. Potential energy surface for asymmetric tautomer II calculated by the MNDO–AM1 method

dipole moment, in our case equal to 2·16 D, which is much lower than the experimentally determined values (cf. Dipole moment section). One can expect a better agreement if one takes into account the influence of the Onsager reaction field on dipole moments. The calculations were performed with the MOPAC.5 modification implemented by a self-consistent reaction field (SCRF).[19] One of the parameters of this model is the Onsager sphere radius. From earlier calculations,[28] it was found that the best value is calculated from the volume occupied by a molecule in a crystal structure. In the case of DPhG, the radius calculated in such a way is 4·11 Å. Calculations performed with this radius and the permittivity of CCl_4 give some modifications of the structure and dipole moment. The results obtained are given in Table 1. It has been stated that both applied methods should not make, on average, a mistake in dipole moment determinations higher than 0·48 and 0·38 D for AM1 and PM3, respectively.[18]

Considering this and the uncertainty of the extrapolation procedure, one can mention that all the calculated average dipole moments, except by AM1 for tautomer **II**, are substantially lower than the corresponding experimental values. The conclusion concerning applied semi-empirical methods can be that the MNDO–AM1 method reproduces better than MNDO-PM3 the dynamic conformation of DPhG in non-polar solvents.

Calculations confirm the spectroscopic measurements results, that we have to deal with the tautomer **II** for a free molecule (presumably also in low-polarity solutions), as was found in the solid-state structure and water and DMSO solutions.[29]

Very detailed calculations on the structure of diphenylguanicline and its monocation have been performed recently by Alagona *et al.*[30] at the molecular mechanics and *ab initio* level with the aim of explaining the biological activity of DPhG in aqueous solutions. A high sensitivity of the calculated distribution of conformers to the character of the applied methods and corrections such as the basis set, solvent interaction, MP2 corrections and free energy of cavitation was reported. These calculations were performed only for tautomer **I**. As far as we can compare our results with those obtained by Alagona *et al. in vacuo*, taking into account the differences in conformers we found that most of the *ab initio*-calulated conformers do not fall in the minima region calculated by the semi-empirical methods for conformer **I** (Figures 5 and 7). Further studies considering also other structural parameters may explain the source of these discrepancies.

CONCLUSIONS

The dipole moment and average molecular weight of *N,N'*-diphenylguanidine were determined in non-polar solvents as a function of concentration. These measurements indicated that in range of concentrations studied cyclic dimers are formed. The IR spectra and results of average molecular weight measurements showed that the association can be described by an association constant of $190 \pm 7\ dm^3 mol^{-1}$ in CCl_4 solution, K_{eq} decreasing with increase in solvent polarity. Generally, this can be understood as a result of competition between dimer formation and interaction with a solvent. Different models of the cyclic dimer structure were proposed for two possible tautomers of the studied compound. The IR spectra showed that the basic group active in hydrogen bond formation is the C=N—Ph group and the acidic part of the complex is the —N(Ph)H group. The results indicate that the cyclic dimer has the structure **IIIc** shown in Scheme 2. On the basis of the IR spectra and PM3 and AM1 semi-empirical calculations, the asymmetric tautomer *II* was suggested as the predominant form in non-polar solvents. This is the same form as was found in the solid state.

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