THEORETICAL AND EXPERIMENTAL DIPOLE MOMENTS OF PURINES[+]

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As a follow-up on our previous study of a series of purines (purine, 6-chloropurine, purine-6-thiol, hypoxanthine, theobromine, theophylline, caffeine, and uric acid), we have investigated six additional biologically important purines (adenine, guanine, isoguanine, thioguanine, xanthine, and kinetin). Their ground-state dipole moments were measured in dioxane at 293 K. The first excited singlet-state dipole moments were obtained using the solvatochromic shift equations (McRae, Suppan, Bakhshiev, and Kawski–Chamma–Viallet). The theoretical dipole moments were calculated as a combination of the π-moment (PPP method) and the σ-moment (vector sum of the σ-bond and σ-group moments). The same approach was used to obtain their first excited singlet-state dipole moments (excited state π-moment; σ-moment assumed to be the same as in the ground state). *Ab initio* HF 6-31G** calculations were also used to obtain ground-state dipole moments for all the fourteen purines under study. In addition, a DFT/B3PW91/6311++(2df,2p) calculation has been carried out for purine for comparison. The different sets of theoretical dipole moments were compared with the respective experimental values. There is an approximately equally good agreement among the experimental dipole moments and the PPP + σ dipole moments (±6.9%) and the *ab initio* dipole moments (±7.4%). The effect of structure on the dipole moments is discussed.

Keywords: Purines; Theoretical and experimental dipole moments; *Ab initio* calculations; PPP method; DFT method; Solvatochromic shift equations; Electronic absorption; UV spectroscopy.

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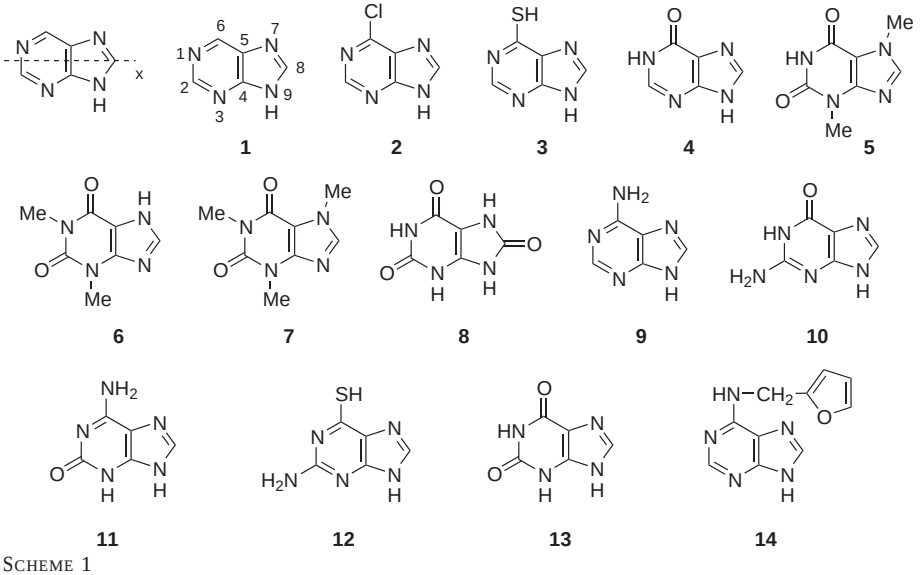
In one of our previous publications devoted to ground- and excited-state dipole moments of aromatic heterocycles, we reported the experimental and calculated dipole moments of a series of biologically important purines[1]. The original study included purine (**1**), 6-chloropurine (**2**), purine-6-thiol (**3**), hypoxanthine (**4**), theobromine (**5**), theophylline (**6**), caffeine (**7**), and uric acid (**8**). Very little has been published on the ground-state dipole moments of purines, especially because of their poor solubility in nonpolar solvents[2–7]. No experimental excited-state dipole moments have appeared in the literature, mainly because of the low fluorescence quantum yields of the purines[8,9].

This contribution is devoted to a similar study of the remaining biologically important purines and complements our previous paper on this topic[1]. The purines included in the current study were adenine (**9**), guanine (**10**), isoguanine (**11**), thioguanine (**12**), xanthine (**13**), and kinetin (**14**). Adenine (**9**) and guanine (**10**) are the purine bases in nucleic acids (DNA and RNA) and adenine is also found in coenzymes such as codehydrase I and II and co-alanine dehydrase. Isoguanine (**11**) is isomeric with guanine (**10**) and its β-ribofuranoside has been isolated from croton beans. After purine-6-thiol (**3**), thioguanine (**12**) is the second most widely used antineoplastic drug in the purine series. Xanthine (**13**) is an alkaloid found in potatoes, coffee beans, and tea. It is also present in animal organs and yeast and it was isolated from urinary bladder stones. Kinetin (**14**) is a well-known cell growth division factor found in various plants and yeast.



SCHEME 1

We wish to report our results obtained for the calculated and experimental ground-state and the first excited singlet-state dipole moments of the purines **1**–**14**, and to compare them with some of our previously published results for the first series of purines, **1**–**8** (Scheme 1). Furthermore, in this contribution we wish to present *ab initio* calculations of the dipole moments for all the purines under study, **1**–**14**, and to compare them with our second series of calculated dipole moments obtained as a combination of the π-component (PPP calculations) and the σ-component (vector sum of the σ-bond and σ-group moments).

EXPERIMENTAL

Chemicals

Adenine used in this study was obtained from Fluka AG (Buchs, Switzerland). Guanine, thioguanine, xanthine, and kinetin were commercial products obtained from Aldrich Chemical Company (Milwaukee (WI), U.S.A.). Isoguanine was purchased from Pfaltz and Bauer (Waterbury (CT), U.S.A.). The formulas of the purines under study are shown in Scheme 1. Analytical or spectroscopic grade solvents were used to prepare the solutions.

Instrumentation

Ultraviolet absorption spectra of the purines were determined at room temperature (293 K) on a Varian DMS spectrophotometer. Fluorescence spectra were taken at room temperature using a Perkin–Elmer LS-5 spectrophotofluorometer.

The permittivities (D) (subsequently converted into dipole moments) were measured in dioxane at 293 K on a dipole meter DM-01 (Wissenschaftlich-Technische Werkstätten, Weilheim, Germany). The refractive indices (n) were obtained with an Abbé refractometer (Bausch and Lomb, Rochester (NY), U.S.A.).

The calibration of the dipole meter was carried out with six different solvents ranging from hexane to dibutyl ether. The regression line obtained for a plot of the permittivity of the solvent *vs* scale reading was $D = 0.001 \times$ scale reading + 0.0664, correlation coefficient $r = 0.999$. For each compound, seven points (including the point for the pure solvent) were used in the linear regression plotting the permittivities and the refractive index *vs* the weight fraction.

Measurements

The experimental ground-state dipole moments (μ_g) of purines were evaluated according to the formula[10–12]

$$\mu_g^2 = [(27kT)/(4\pi N)]\{1/[d(D + 2)^2]\}(A_D - A_n)M \,, \qquad (1)$$

where k is the Boltzmann constant ($1.381 \cdot 10^{-23}$ J deg^{-1}), T is the absolute temperature, N is the Avogadro number ($6.023 \cdot 10^{23}$ mol^{-1}), d and D are the density and permittivity of the

solvent, respectively, A_D and A_n are the numerical values obtained from the solute permittivity and refractive index measurements, respectively, and M is the molecular weight of the solute.

For fluorescent compounds, two formulas were used for the treatment of solvent spectral shifts to determine the excited-state dipole moments of purines: Bakhshiev formula[13] and Kawski–Chamma–Viallet formula[14–16]. For nonfluorescent compounds, McRae formula[17,18] and Suppan formula[19,20] were used.

The general form of the above-mentioned solvatochromic equations is:

$$f(\nu) = sF + q \,. \qquad (2)$$

For fluorescent compounds, $f(\nu)$ is either $\nu_A - \nu_F$ (Bakhshiev) or $(\nu_A + \nu_F)/2$ (Kawski–Chamma–Viallet) where ν_A and ν_F are the absorption and emission maxima wavenumbers (in cm^{-1}), respectively. For nonfluorescent compounds, $f(\nu) = \nu_A$ (McRae and Suppan). On the right-hand side of the equation, s is the slope of a regression line, F is the solvent function whose form depends on the respective solvatochromic equation used, and q is the intercept with the y-axis. In the Bakhshiev and Kawski–Chamma–Viallet formulas, the expression for F (F_1 and F_2, respectively) is based on the solvent dielectric constant, D, and its index of refraction, n. In the McRae and Suppan formulas (F_3 and F_4), it is based strictly on the solvent dielectric constant. The expression for the slope, s, contains the ground and singlet excited state dipole moment, the solute cavity radius (Onsager), Planck constant, and the velocity of light. Again, its exact form depends on the respective solvatochromic equation employed. From the slope of a linear plot (regression line) of $f(\nu)$ *vs* F, it is possible to evaluate the first excited singlet-state dipole moment on the basis of the knowledge of the ground-state dipole moment and the value of s.

These formulas and a detailed discussion of their use can be found in our previous publications[21–23].

The values of solute cavity radii (a_0) needed for these equations were calculated from the molecular volume of the purines according to Suppan's equation[24]:

$$a_0 = (3M/4\pi dN)^{1/3}, \qquad (3)$$

where d is the solid-state density of the solute molecule and the meaning of the remaining symbols is the same as in Eq. (*1*). The solid-state densities of the purines, d, were determined pycnometrically at room temperature (295 K), in the form of a suspension of the respective purine (200 to 600 mg) in kerosene ($d_4^{22} = 0.786$). The results are summarized in Table I.

The values of solvent functions, $F_1 - F_2$, used in the above solvatochromic equations, can be found for selected solvents in our previous publications[22,25], the values of F_3 and F_4 can be found in references[21,22].

THEORETICAL CALCULATIONS

All semiempirical calculations were carried out on a Hewlett–Packard HP 150 II Touchscreen computer with an 8087 coprocessor, using the standard version of the PPP (Pariser–Parr–Pople, π-LCI-SCF-MO) method[26,27]. In the calculation of the total dipole moments, μ_t, we have combined the use of the PPP method with the empirical σ-bond moment model[28–31]. The π-con-

tributions, μ_π, were obtained by the PPP method using the Mataga–Nishimoto formula for the bicentric electronic repulsion integrals[32]. The parameters used in the calculations were those tested and employed in our previous work[33]. An example of their use for aromatic azaheterocycles can be found in our contribution on a series of indoles[34]. The electronic absorption spectra of selected purines and pyrimidines are discussed in ref.[35]. The σ-contributions, μ_σ, were obtained from the bond dipole moments and group dipole moments[28–31,33]. The total dipole moments, μ_t, were calculated as a vector sum of the π- and σ-components, similarly as in our previous publications[36].

In the calculations of the first excited singlet-state dipole moments, $\mu_{S(1)}$, it was assumed that the change from the ground-state dipole moment was the result of a change in the π-contribution while the σ-contribution was expected to remain the same as in the ground state. In the case of the π-contribution, calculated by the PPP method, it was assumed that the most important part was represented by the $1\rightarrow1'$ (HOMO→LUMO) $\pi\rightarrow\pi^*$ transition. This approach has been successful in our treatment of other heterocyclic compounds[36].

The calculated and experimental ground-state dipole moments of the purines **9**–**14** are presented in Table II while the dipole moments of the purines **1**–**8** can be found in our previous publication[1]. Table III presents the respective first excited singlet-state dipole moments, calculated and experimental.

Information about the calculated first excited triplet-state dipole moments of selected purines can be found in refs[5,40].

TABLE I
Solid-state densities (d_4^{22}) and the Onsager cavity radii (a_0) of the purines **9**–**14**

No.	Compound	Formula (M.w.)	d_4^{22} [a]	a_0 [b], Å
9	Adenine	$C_5H_5N_5$ (135.1)	1.379	3.39
10	Guanine	$C_5H_5N_5O$ (151.1)	1.789	3.22
11	Isoguanine	$C_5H_5N_5O$ (151.1)	1.786	3.22
12	Thioguanine	$C_5H_5N_5S$ (167.2)	1.316	3.69
13	Xanthine	$C_5H_4N_4O_2$ (152.1)	1.616	3.34
14	Kinetin	$C_{10}H_9N_5O$ (215.2)	1.647	3.73

[a] Determined pycnometrically (see Experimental). [b] Calculated by Suppan formula[24], see Eq. (*3*).

TABLE II
Calculated and experimental ground-state dipole moments (D) of the purines **9**–**14**[a]

No.	Compound	μ_{calc}[b], D	θ[c], °	μ_{exp}[d], D
9	Adenine	3.659[e]	168	3.85[f]
10	Guanine[g]	8.366[h]	52	5.50
11	Isoguanine[i]	9.438	167	6.37
12	Thioguanine	2.776	85	3.33
13	Xanthine	8.659	113	4.46
14	Kinetin	3.669	179	5.46

[a] For the dipole moments of the first series of purines, **1**–**8**, see ref.[1] [b] π-Moment (PPP method) + σ-moment (vector sum of σ-bond and group moments). [c] Angle between the positive direction of the *x*-axis and the positive direction of the dipole moment read counterclockwise (for the orientation of the structures, see Scheme 1). [d] In dioxane. Accuracy: ±10%. [e] Literature[37] gives 3.61 D, IEHT calculation. Other calculated values range from 2.0 to 5.1 D [38]. [f] Literature[39] gives 3.0 D (also for 9-methyladenine). [g] Enol form: μ_{calc} 8.21 D, θ 344°. [h] Literature[37] gives 8.73 D, IEHT calculation. Other calculated values range from 6.15 to 16.5 D [38]. [i] Enol form: μ_{calc} 7.220 D, θ 51°. [j] A simplified model of kinetin was used in the calculation.

TABLE III
Calculated and experimental first excited singlet-state dipole moments (D) of the purines **9**–**14**[a]

No.	Compound	$\mu_{S(1)}$(calc)[b], D	$\theta_{S(1)}$[c], °	$\mu_{S(1)}$(exp), D			
				I[d]	II[e]	III[f]	IV[g]
9	Adenine	5.521[h]	171	–	–	5.70	9.35
10	Guanine[i]	3.541[j]	60	–	–	0.26	[k]
11	Isoguanine	10.169	133	[l]	[l]	2.73	[k]
12	Thioguanine	5.844	79	7.11	[l]	19.77	9.19
13	Xanthine	11.731	113	10.47	3.11	[k]	[k]
14	Kinetin	5.954	172	–	–	5.88	6.51

[a] For the first excited singlet-state dipole moments of the first series of purines, **1**–**8**, see ref.[1] However, because of an error in the equation used, the Bakhshiev correlations found in ref.[1], Table 9, p. 132 (column marked as I) are incorrect and should not be used. Column II (Chamma–Viallet) is correct. [b] π-Moment (PPP method, S_1 state) + σ-moment (the σ-moment is the same as in the ground state). [c] Angle between the positive direction of the *x*-axis and the first excited singlet-state dipole moment read counterclockwise. [d] Bakhshiev correlations. [e] Kawski–Chamma–Viallet correlations. [f] McRae correlations. [g] Suppan correlations. [h] Literature[40] gives 3.26 D, VE-PPP calculation. Other calculated values: 2.0 D (CNDO/s-CI)[40], 3.134 D [5]. [i] Enol form: $\mu_{S(1)calc}$ 7.621 D, $\theta_{S(1)}$ 12°. [j] Literature[41] gives 3.4 D. Other values: 3.746 D [5], 4.3 D (CNDO/s-CI)[40], 6.67 D (VE-PPP)[40]. [k] A negative dipole moment value was obtained. [l] No correlation.

The *ab initio* ground-state dipole moments of the purines, **1–14**, were obtained at the HF (Hartree–Fock) 6-31G** level of theory applying the *ab initio* program SPARTAN (version 4.1.1, Wavefunction, Inc., 18401 Von Karman Ave., 370, Irvine, CA 92715). An additional calculation for purine (**1**) was performed using the DFT/B3pW91/6311++G(2df,2p) method. A comparison of the two values for purine (3.66 D (HF) and 3.70 D (DFT)) indicates an excellent agreement.

The *ab initio* calculations have been carried out on different workstations (CHALLENGE L (Silicon Graphics), DEC3000/300AXP, and DEC Alpha 2000 5/250).

A comparison of the theoretical ground-state dipole moments, both *ab initio* and those obtained by the PPP method + σ-contributions, with the experimental values is presented in Table IV.

TABLE IV
Ab initio calculated dipole moments (D) of purines and their comparison with the PPP + σ-contribution calculated and experimental values[a]

No.	Compound	μ (*ab initio*)[b]	Components	$\mu_{PPP+\sigma}$[c]	μ_{exp}[d]
1	Purine	3.662[e]	*x* = 2.1183	4.35[f]	2.92 (AcOEt)
			y = 0.0000		4.32 (dioxane)
			z = 2.9875		
2	6-Chloropurine	4.977	*x* = –0.1357	4.58[g]	3.89 (AcOH)
			y = 0.0000	5.87[h]	5.34 (dioxane)
			z = 4.9751		
3	Purine-6-thiol	3.388	*x* = 0.1064	3.79[i]	3.59 (AcOH)
			y = 0.0000		
			z = 3.3860		
4	Hypoxanthine	5.605	*x* = 5.5250	2.78[j]	3.16 (AcOH)
			y = 0.0000	6.26[k]	
			z = 0.9468		
5	Theobromine	5.043	*x* = 1.3247	4.14	3.11 (AcOH)
			y = –0.0563		
			z = 4.8660		
6	Theophylline	4.048	*x* = 1.2366	4.64[l]	2.70 (AcOH)
			y = –0.0428		3.88 (AcOEt)
			z = 3.8544		3.94 (dioxane)
7	Caffeine	4.350	*x* = 0.8041	4.58	3.59 (AcOEt)
			y = –0.0581		3.70 (C_6H_6)
			z = 4.2750		3.83 (AcOH)
					4.6 (dioxane)

TABLE IV
(*Continued*)

No.	Compound	μ (*ab initio*)[b]	Components	$\mu_{PPP+\sigma}$[c]	μ_{exp}[d]
8	Uric acid	3.200	*x* = 3.1854 *y* = 0.0000 *z* = –0.3092	4.03	[m]
9	Adenine	2.470	*x* = –0.0490 *y* = 0.1866 *z* = 2.4628	3.659	3.85 (dioxane)
10	Guanine	6.835	*x* = 5.9190 *y* = 1.0082 *z* = 6.9911	8.366	5.50 (dioxane)
11	Isoguanine	7.381	*x* = 2.2051 *y* = 0.8595 *z* = 1.6618	9.438 7.220[n]	6.37 (dioxane)
12	Thioguanine	4.046	*x* = 3.5537 *y* = 0.9911 *z* = 1.6618	2.776	3.33 (dioxane)
13	Xanthine	7.651	*x* = 6.9639 *y* = 0.0000 *z* = 1.6618	8.659	4.46 (dioxane)
14	Kinetin	–	–	3.669	5.46 (dioxane)

[a] Ground-state values. [b] For details concerning the *ab initio* calculations, see the text (Experimental, Theoretical Calculations). [c] *Cf.* Table IV for purines **9**–**14**; for purines **1**–**8**, see ref.[1] [d] The solvent is shown in parentheses. [e] Our DFT value is 3.70 D. [f] 9*H*-Purine. For 7*H*-purine, the value is 6.33 D. [g] 6-Chloro-7*H*-purine. [h] 6-Chloro-9*H*-purine. [i] 9*H*-purine-6-thiol. The value for the 7*H*-isomer is 6.49 D. [j] 7*H*-Hypoxanthine. [k] 9*H*-Hypoxanthine. [l] 7*H*-Theophylline. 9*H*-Theophylline has 7.66 D. [m] Not determined because of poor solubility. [n] Enol form: 7.220 D.

RESULTS AND DISCUSSION

Theoretical and Experimental Ground-State Dipole Moments

The theoretical and experimental dipole moments of the purines under study, **9**–**14**, are presented in Table IV, along with the appropriate angles showing their direction. The values of calculated dipole moments listed in this table were obtained as a combination of the π-moment (PPP method) and the σ-moment (from σ-bond and group moments). While there is a very good agreement between the theoretical and experimental dipole moments of adenine (**9**; 3.659 and 3.85 D, respectively) and an acceptable agreement for thioguanine (**12**; 2.776 and 3.33 D, respectively), a comparison of the values for the remaining compounds indicates that there are dis-

crepancies between the two sets of values. Additional theoretical values for adenine (**9**) and guanine (**10**) available in the literature cover a wide range: from 2.0 to 5.1 D for adenine (**9**) and from 6.15 to 16.5 D for guanine (**10**) due to the method of calculation. For guanine, there is a relatively good agreement between the theoretical dipole moment of 6.15 D (obtained by the CNDO/s-CI method) and the actual experimental value of 5.50 D. Some of the possible reasons why the agreement between the theoretical and experimental dipole moments is not better are outlined below.

The solubility of the purines used in this study (**9**–**14**) is quite poor making the experimental determination of the dipole moments difficult. In the case of the first series of the purines, **1**–**8**, the agreement was much better and there is no question that their somewhat better solubility in the solvents used contributed to this better outcome[1]. There is a possibility of keto-enol tautomeric equilibria in some of the substituted purines. As an example, theoretical studies of tautomerism in several purines are available, but experimental information for solutions of purines is limited[42–48]. Finally, as the spread of the theoretical values shows, they depend on the method used in the calculations. The first excited singlet-state counterparts of these ground-state dipole moments can be found in Table III and will be addressed later.

Table IV presents a comparison of the ground-state dipole moments computed by an *ab initio* (HF) method, with optimized geometries (SPARTAN, version 4.1.1), with the results of our semiempirical calculations (for **1**–**8**, see ref.[1]; for **9**–**14**, see Table IV) obtained by the PPP method, with the σ-contribution added as a vector sum of the σ-bond and group moments, and with the experimental dipole moments. It is interesting to note that, while in some cases the agreement between theoretical and experimental moments is approximately equally good for *ab initio* and PPP calculations, it is not always the case. In general, *ab initio* calculations do not offer a significantly better agreement than the PPP method, although they are superior from the physical point of view. In applicable cases, the difference between the experimental dipole moments and PPP + σ dipole moments is typically ±6.9%, while the difference between the experimental and the *ab initio* dipole moments is ±7.4%.

Solvent Effects on the Electronic Absorption and Fluorescence Spectra

The electronic absorption spectra of all the purines under study were investigated in several solvents of different polarity, including dioxane, tetrahydrofuran, ethyl acetate, ethylene glycol, ethanol, dimethylform-

amide, acetonitrile, and dimethyl sulfoxide. Examples are given in Figs 1 and 2. Two different types of behavior, depending on the molecular structure of the respective purine derivative, can be observed (Table V). In the case of adenine (**9**) and kinetin (**14**), the absorption band maxima are slightly red-shifted when going from a low-polarity solvent, such as diethyl ether, to a strongly polar solvent such as dimethyl sulfoxide, indicating that the longest-wavelength band of these purines is due to a $\pi \rightarrow \pi^*$ transition. This assignment is confirmed by the fact that the molar absorption coefficient values are larger that 10^4 l mol^{-1} cm^{-1} in most solvents. On the other hand, the absorption spectra of guanine (**10**), isoguanine (**11**), thioguanine (**12**), and xanthine (**13**) are blue-shifted when going from solvents with a low permittivity (dioxane, diethyl ether) to highly polar solvents (dimethylformamide, dimethyl sulfoxide). Furthermore, the molar absorption coefficients are significantly smaller than for the former two compounds. It is possible that an $n \rightarrow \pi^*$ transition appears in the long-wavelength absorption band of these purines.

Only three purines under study, *i.e.*, isoguanine (**11**), thioguanine (**12**), and xanthine (**13**), give fluorescence in majority of the solvents used

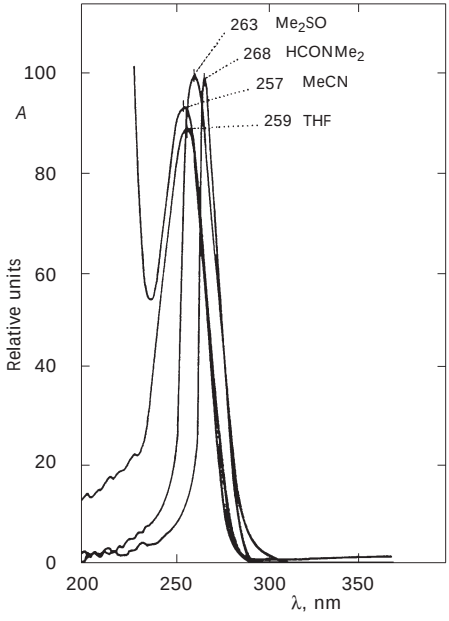


FIG. 1
Solvent effect on the electronic absorption spectrum of adenine

(Table V). In the case of thioguanine (**12**), no significant shift of the fluorescence emission maximum is observed on changing the solvent, whereas in the case of isoguanine (**11**) and xanthine (**13**), the fluorescence maxima are blue-shifted with increasing solvent polarity.

TABLE V
Statistical treatment of the correlations of solvent electronic absorption spectral shifts of the purines **9**–**14**

No.	Compound	Slope	Intercept, cm^{-1}	Correlation coefficient, *r*	Number of points, *n*
		McRae correlations			
9	Adenine	–924	39 884	0.952	5
10	Guanine	4 331	29 465	0.951	5
11	Isoguanine	3 478	27 816	0.945	6
12	Thioguanine	–5 475	38 919	0.987	7
13	Xanthine	3 465	30 843	0.978	6
14	Kinetin	–224	37 876	0.991	5
		Suppan correlations			
9	Adenine	–2 744	40 287	0.944	5
10	Guanine	10 922	27 024	0.955	5
11	Isoguanine	10 350	24 307	0.944	6
12	Thioguanine	1 952	26 975	0.949	7
13	Xanthine	10 262	27 406	0.978	6
14	Kinetin	–558	38 003	0.978	5
		Bakhshiev correlations[a]			
11	Isoguanine[b]	–	–	–	–
12	Thioguanine	286	2 940	0.992	6
13	Xanthine	9 740	–1 140	0.989	4
		Kawski–Chamma–Viallet correlations[a]			
11	Isoguanine	43 548	858	0.919	7
12	Thioguanine[b]	–	–	–	–
13	Xanthine	4 531	30 336	0.999	4

[a] For compounds **9**, **10**, and **11**, the number of data was too small to obtain meaningful plots. [b] No correlation.

Excited-State Dipole Moments

Table V presents the first excited singlet-state dipole moments of the purines **9**–**14** obtained from the slopes of the McRae, Suppan, Bakhshiev, and Kawski–Chamma–Viallet solvatochromic correlations. Examples of solvatochromic correlations are shown in Figs 3 and 4 for adenine and in Figs 5

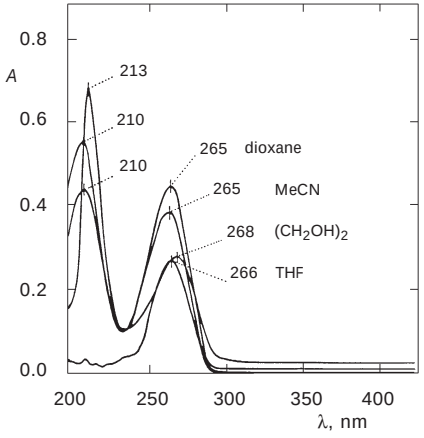


FIG. 2
Solvent effect on the electronic absorption spectrum of kinetin

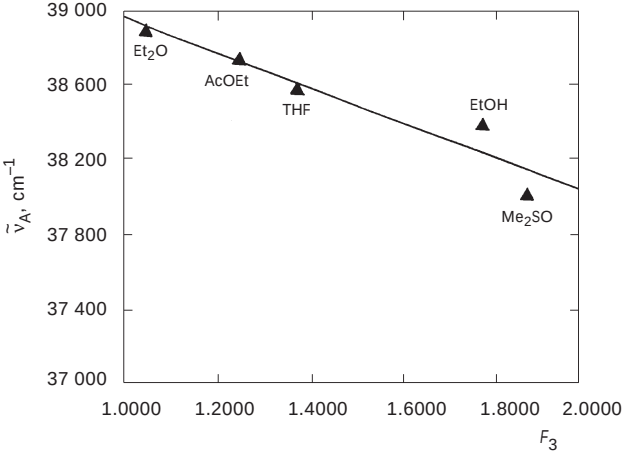


FIG. 3
McRae correlation between solvent chemical shifts and F_3 solvent terms for adenine (**9**)

and 6 for kinetin. Only the McRae and Suppan correlations could be used for nonfluorescent compounds. As already noted in our previous publications[21,36], numerous assumptions and approximations have to be made when determining the experimental or computing the theoretical values of excited-state dipole moments. This, in general, accounts for the discrepan-

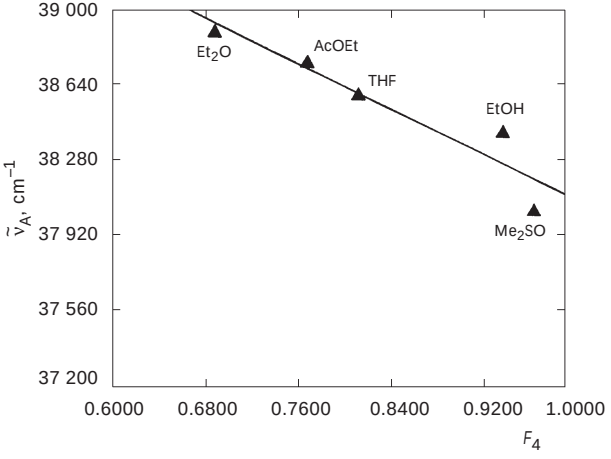


FIG. 4
Suppan correlation between solvent spectral shifts and F_4 solvent terms for adenine (**9**)

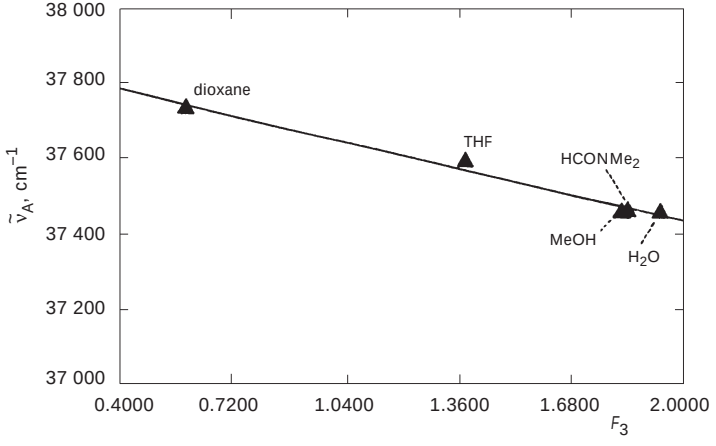


FIG. 5
McRae correlation between solvent spectral shifts and F_3 solvent terms for kinetin (**14**)

cies between calculated and experimental excited-state dipole moments and among the values of experimental moments obtained by using different solvatochromic equations.

Inspection of the data in Table III shows a good or acceptable agreement between our calculated first excited singlet-state dipole moments and the experimental values for adenine (**9**; 5.521 *vs* 5.70 D, McRae), thioguanine (**12**; 5.844 *vs* 7.11 D, Bakhshiev), xanthine (**13**; 11.731 *vs* 10.47 D, Bakhshiev), and kinetin (**14**; 5.954 *vs* 5.88 D, McRae and 6.51 D, Suppan). No good correlations were obtained for guanine (**10**) and isoguanine (**11**) and, of course, some of the values do not correlate well, *i.e.*, even if one solvatochromic equation gives a good value, others do not.

A comparison of the ground-state dipole moments (Table II) and the first excited singlet-state dipole moments (Table III) for compounds **9**–**14** reveals that, in three cases (adenine, thioguanine, kinetin), their first excited singlet-state dipole moment is higher than in the ground state, whereas the remaining purines (guanine, isoguanine, xanthine) possess lower excited-state dipole moments than their ground-state counterparts. In the first series of purines discussed in our previous publication[1], most compounds have a lower experimental excited-state dipole moment than the respective ground-state dipole moment. The only exception is 6-chloropurine (**2**).

We have not addressed excited triplet-state dipole moments in this contribution. Limited information about calculated first excited triplet-state dipole moments of selected purines is available[5,40].

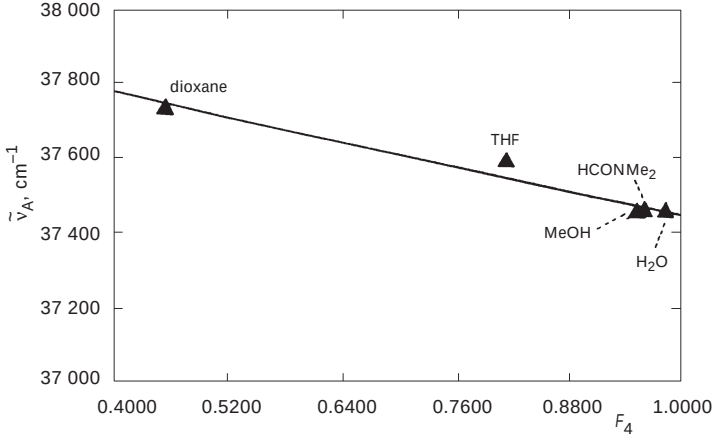


FIG. 6
Suppan correlation between solvent spectral shifts and F_4 solvent terms for kinetin (**14**)

Effect of Structure on Dipole Moments

It seems worthwhile to compare the effect of substituents on the dipole moments of purines in their ground and first excited singlet states. The sequence of dipole moments in the purine series is as follows: in the ground state, thioguanine < purine < adenine < xanthine < kinetin < guanine < isoguanine; in the first excited singlet state, guanine < isoguanine < purine ≈ xanthine < adenine ≈ kinetin < thioguanine (*cf.* Tables II and III).

The inversion of the order of dipole moments in the excited state with respect to the ground state can be explained in terms of an increase in the excited singlet-state dipole moments of adenine (**9**) and thioguanine (**12**) and a significant decrease in the excited-state dipole moments of guanine (**10**) and isoguanine (**11**). This seems to indicate that the electron-donating interactions of the amino and thiol groups (present in adenine and thioguanine, respectively) with the heteroaromatic π-system are enhanced in the excited state, resulting in a more marked partial electric charge separation. Apparently, the electron-withdrawing effect of the carbonyl groups acts in an opposite way in guanine (**10**) and isoguanine (**11**).

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