Molecular Conformation and Electronic Structure of Azomethines. Part 6.[1a] Electronic Spectra of *N*-Benzylidenemethylamines

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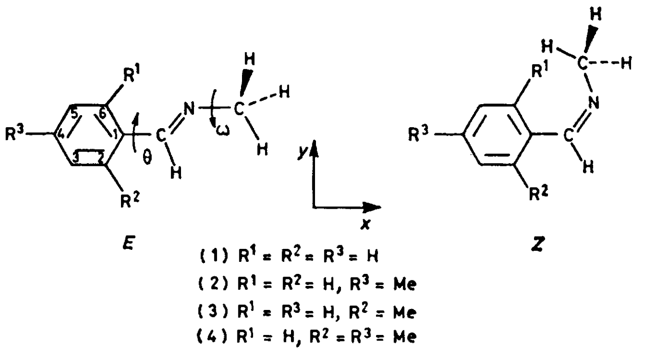
The electronic spectra of some methyl derivatives of *N*-benzylidenemethylamine have been measured in the vapour phase and in various solvents. For the *N*-benzylidenemethylamine, CNDO/2 calculations confirm a coplanar *E*-configuration with the hydrogen atom of the *N*-methyl group eclipsed by the C=N double bond. The theoretical interpretation of the electronic spectra using CNDO*CI and P calculations is in line with the configurational and conformational results previously obtained by dipole moment analysis.

BENZALDEHYDE shows the first π–π* charge-transfer band at *ca.* 240 nm; introduction of a methyl substituent into the benzene ring causes a bathochromic shift of the charge transfer band. However, the magnitude of the shift caused by an *o*-methyl is considerably smaller than that caused by a *p*-methyl substituent. In addition, the intensity of the charge transfer band of the *o*-methyl compound is smaller than that of the *p*-methyl compound.[2] The difference between these effects is attributed, partly at least, to the effect of the *o*-substituent which will hinder the benzene ring and the carbonyl group from assuming a coplanar arrangement.

The electronic spectrum of *N*-benzylidenemethylamine is similar to that of benzaldehyde.[3] The size of the bathochromic shift caused by the introduction of methyl substituents should indicate if the steric hindrance of the *o*-methyl with the azomethine group is higher or lower than that with the carbonyl fragment. However, in aldimines *E–Z* isomerism is possible with a sufficiently large barrier of interconversion. The equilibrium distribution of *E–Z* isomers has been analysed by n.m.r. techniques.[4] The preferred ground-state conformation is a compromise between the conjugative stabilization of the coplanar conformations and the steric interaction of the *ortho*-substituents with the vinyl hydrogen (in the *E*-isomer) or the *N*-methyl group (in the *Z*-isomer).

In the present work we report a theoretical interpretation of the electronic spectra of *N*-benzylidenemethylamine and of some methyl derivatives (see Scheme) based on the configurational and conformational results suggested for these derivatives by dipole moment analysis.[1]



(1) $R^1 = R^2 = R^3 = H$
(2) $R^1 = R^2 = H$, $R^3 = Me$
(3) $R^1 = R^3 = H$, $R^2 = Me$
(4) $R^1 = H$, $R^2 = R^3 = Me$
(5) $R^1 = R^2 = R^3 = Me$

SCHEME

EXPERIMENTAL

Preparation and Purification of Compounds.—The benzylideneamines (1)—(5) were synthesized and purified as previously reported.[1] Physical and microanalytical data for the *imine* (5) are: b.p. 120—121 °C at 17 Torr; $\nu_{max.}$ 1 680 and 1 640 cm^{-1} (Found: C, 81.9; H, 9.6; N, 8.6. $C_{11}H_{15}N$ requires C, 81.9; H, 9.4; N, 8.7%).

Dipole Moment.—The dipole moment of the imine (5) was determined as described previously for derivatives (1)—(4).[1b] The measured properties of the solutions at 25.0 °C together with the polarization data and the dipole moment are given in Table 1; the symbols have their usual meanings.

TABLE 1

Dipole moment measurements for *N*-2,4,6-trimethylbenzylidenemethylamine at 25 °C in benzene solution *

10^5w	$10^5(\varepsilon_{12} - \varepsilon_1)$	$10^5(n_{12}^2 - n_1^2)$	
198	375	60	
319	495	90	
459	701	120	α 1.79 ± 0.05
608	1 043	180	β 0.299 ± 0.006
686	1 195	210	μP_2/cm^3 45.12
950	1 566	270	μ/D 1.49 ± 0.03
1 083	2 016	330	

* w = Weight fraction; errors in α and β are quoted as ± probable errors and based on the least-squares plot; these errors are combined to give the quoted error in μ.

Electronic Absorption Spectra.—The spectra of the compounds dissolved in anhydrous methanol and ethanol[5] as well as in n-hexane and cyclohexane Spectrograde reagents were measured. Care was taken to shield the solutions from exposure to light, and the absence of any hydrolysis products was checked. Absorption in solution was measured by a Cary 118 spectrophotometer over the 200—360 nm range, for 10^{-3}, 10^{-4}, and 10^{-5}M solutions in silica cells with optical paths of 0.1, 1, and 10 cm. Vapour phase spectra were recorded on a Hitachi–Perkin-Elmer model 124 spectrophotometer, as previously reported.[6] The wavelengths of absorption maxima of imines (1)—(5) in solution and in the vapour phase, together with their extinction coefficients are given in Table 2. Experimental spectra in cyclohexane as well as f values evaluated through the relationship $f = 4.32 \times 10^{-9}\ \Delta\nu_{1/2}\ \varepsilon_{max.}$ were compared with those simulated from theoretical values.

CALCULATIONS

Two approaches were followed in the theoretical interpretation of the electronic spectra and the dipole moments of our derivatives.

In the first one, a CNDO/2 calculation[7] for the ground-

TABLE 2

Electronic spectra of benzylidenemethylamines [a]

	Vapour		n-Hexane		Cyclohexane		Methanol		Ethanol	
Compd.	λ/nm	Intensity ratio	λ/nm	ε	λ/nm	ε	λ/nm	ε	λ/nm	ε
(1)	284	0.055			286	730	(287)	880		
	274	0.058			276	960	(277)	1 330		
	(238)	0.93			(248)	14 600				
	(232)	1.00			243	16 300	244	15 000		
(2)	285	0.072			290	880	291	1 850		
	276	0.095			280	1 270	(282)	2 350		
	(246)	0.91			(257)	14 500				
	240	1.00			251	17 200	253	18 500		
					213	16 100				
(3)	(292)	0.10	(296)	960	(296)	910				
	283	0.11	285	1 390	286	1 310	286	1 590	286	1 470
	275	0.08	278	1 350	279	1 270				
	242	0.92	248	12 500	(248)	12 900				
	238	1.00	244	13 000	244	13 500	248	12 400	248	12 000
	198	1.50	206	27 500	208	26 000	206	23 500	206	23 100
(4)	(294)	0.16	297	1 050	297	1 050	(297)	1 460	(298)	1 600
	(285)	0.18	286	1 540	286	1 650	(287)	2 310	(288)	2 480
	244	1.00	250	16 900	251	17 800	256	13 200	256	15 300
	206	1.42	212	26 100	(212)	27 700				
			209	26 500	209	27 900	208	20 200	209	22 900
(5)	(300)	0.10	(301)	750	(302)	1 040				
	(280)	0.13	(294)	1 050	(294)	1 230				
	248	1.00	254	14 900	254	14 000	250	9 550	252	8 800
	209	2.01	215	30 000	216	28 000	212	20 100	212	19 600
			(212)	28 000	(212)	26 000	208	20 200	208	20,000

[a] Wavelengths in parentheses denote inflections.

state properties of the *N*-benzylidenemethylamine was carried out and the minimum energy geometry determined. The electronic spectrum for this geometry was calculated by the CNDO/CI method.[8]

In the second one, the calculation of the electronic transitions was performed with the P [9] and CNDO/CI method by taking into account the conformational results obtained by dipole moment analysis in previous work.[1a]

CNDO/2 *Calculations*.—A modified version of the QCPE program no. **141** was used; the total molecular energy was calculated at different values of θ (torsional angle of the phenyl ring) and ω (torsional angle of the *N*-methyl group). The co-ordinate system is shown in the Scheme. Geometrical parameters were: $r_{CC(1)}$ 1.517 − 0.067cos θ,[2] $r_{C=N}$ 1.295, r_{N-C} 1.440, $r_{CC(aromatic)}$ 1.397, $r_{C(sp^2)H}$ 1.08, and $r_{C(sp^3)H}$ 1.09Å; $C=\widehat{N}-Me$ 117°, $N-\widehat{C}-H$ 109.5°, all other valence angles being 120°.

In the *E*-isomer of *N*-benzylidenemethylamine (1) we have considered two different conformations: the first with a hydrogen atom of the *N*-methyl group eclipsed by the C=N double bond (ω 0°) and the second with a hydrogen atom of the *N*-methyl eclipsed by the lone-pair of the nitrogen atom (ω 60°) at different values of θ (θ 0° in the planar conformation). Only the energetically more favoured form with ω 60° was considered in the planar *Z*-isomer of imine (1); for θ ≠ 0°, the value of ω was imposed that makes two hydrogen atoms of the *N*-methyl equally distant from the hydrogen atom of the C(6)–H bond. The main data are reported in Table 3, together with those obtained for derivative (3). The latter were performed in order to verify the height of the rotational barrier (at θ 90°) and will be discussed further.

P *Calculations*.—The parameters adopted are in Supplementary Publications No. SUP 22112 of ref. 1*a*. The *n* electrons of the heteroatom were taken into account and the two electrons for each methyl group were treated by the heteroatom model.

In compound (1) (*E*- and *Z*-isomers) the energies of the π–π* and *n*–π* transitions were calculated at different values of θ (from 0 to 90°); only the *E*-isomer at θ 0° was considered for the *p*-methyl derivative (2), while two planar conformations (θ 0 and 180°) were investigated for the *E*-isomer of derivatives (3) and (4). Finally, the energies of the electronic transitions of compound (5) were calculated for the *E*-isomer at θ 0° and for the *Z*-isomer at θ 0, 40, and 80°.

The transition energies and the oscillator strength values obtained for the first *n*–π* transition and for the lowest energy π–π* transitions are collected in Table 4.

TABLE 3

Conformational energies (in kcal mol⁻¹) and dipole moments by the CNDO/2 method

Compound	Isomer	θ (°)	ω (°)	*E* [a]	μ_x/D	μ_y/D	μ_z/D	$\mu_{tot/D}$
(1)	*E*	0	0	0.0 [b]	−0.442	1.687		1.744
		0	60	0.94	−0.408	1.844		1.888
(1)	*Z*	0	60	48.9	2.355	0.441		2.395
		30	24	11.5	2.124	0.299	−0.120	2.148
		45	18	4.1	2.084	0.350	−0.108	2.116
		60	16	3.4 [b]	2.063	0.415	−0.086	2.106
		75	17	4.0	2.039	0.441	−0.066	2.087
(3)	*E*	0	0	2.8	−0.546	1.840		1.919
		90	0	7.0	−0.573	1.909	0.145	1.999
		180	0	0.0 [b]	−0.536	1.555		1.645

[a] Total energy relative to the most stable conformation of the compound. [b] Most stable conformation of the isomer.

TABLE 4

Calculated energies (eV) and oscillator strengths

Compound	Isomer	θ (°)	P Method $(n–\pi^*)_1$	P Method $(\pi–\pi^*)_1$	P Method $(\pi–\pi^*)_2$	CNDO/CI Method $(n–\pi^*)_1$	CNDO/CI Method $(\pi–\pi^*)_1$	CNDO/CI Method $(\pi–\pi^*)_2$
(1)	*E*	0	4.60	4.67 (0.007)	5.10 (0.72)	4.06 (0.008)	4.57 (0.002)	5.06 (0.66)
		30	4.68	4.73 (0.005)	5.27 (0.64)			
		45	4.74	4.81 (0.003)	5.45 (0.54)			
		60	4.80	4.88 (0.001)	5.69 (0.38)			
		75	4.85	4.94 (0.0003)	5.96 (0.17)			
		90	5.19	4.97 (0.0001)	6.18 (0.0)			
(1)	*Z*	0	4.62	4.66 (0.005)	5.05 (0.56)	3.94 (0.008)	4.59 (0.017)	5.24 (0.50)
		30	4.68	4.73 (0.004)	5.21 (0.50)			
		60	4.79	4.88 (0.001)	5.68 (0.31)			
		90	5.20	4.97 (0.001)	6.19 (0.0)			
(2)	*E*	0	4.61	4.63 (0.003)	4.98 (0.76)	4.10 (0.008)	4.44 (0.008)	4.82 (0.70)
(3)	*E*	0	4.60	4.57 (0.040)	5.05 (0.65)	4.21 (0.008)	4.47 (0.029)	5.03 (0.61)
		180	4.64	4.52 (0.061)	5.02 (0.51)	3.66 (0.008)	4.48 (0.030)	5.12 (0.57)
(4)	*E*	0	4.61	4.55 (0.032)	4.94 (0.70)	4.02 (0.008)	4.36 (0.014)	4.76 (0.68)
		180	4.64	4.50 (0.064)	4.92 (0.56)	3.76 (0.009)	4.40 (0.030)	4.88 (0.64)
(5)	*E*	0	4.66	4.46 (0.020)	4.85 (0.60)			
	Z	0	4.68	4.46 (0.016)	4.82 (0.49)			
		40	4.76	4.58 (0.009)	5.05 (0.40)			
		80	4.89	4.79 (0.0003)	5.59 (0.054)			

CNDO/CI *Calculations*.—A modified version of the QCPE program no. 174 was used; two-centre repulsion integrals were calculated through the Mataga–Nishimoto equation.[10] The transition energies and the oscillator strength values obtained for the first transitions are reported in Table 4.

Simulation of Electronic Specta.—The agreement between measured and calculated spectra was tested by simulation of the absorption spectra as a sum of Lorenz lines associated with each transition. The oscillator strengths were calculated from the equation $f = 4.32 \times 10^{-9}\, \varepsilon_{\text{max.}}\, \Delta\tilde{\nu}_{1/2}$ on the assumption that $\Delta\tilde{\nu}_{1/2} \simeq 4\,630\ \text{cm}^{-1}$. As the computational methods used gave overestimated f values, we calculated the ratio between the experimental f value of the absorption band at 243 nm in the cyclohexane spectra of *N*-benzylidenemethylamine and the corresponding value of the composite spectrum calculated from the P results. The ratio (r 0.428) was used as a correction factor for the theoretical f value of each transition.

DISCUSSION

The previously suggested [1] coplanar *E*-configuration of the *N*-benzylidenemethylamine (1) is confirmed by the results of the present work; moreover, the hydrogen atom of the *N*-methyl group may be considered eclipsed by the C=N double bond. The dipole moment calculated by the CNDO/2 method (1.74 D) is higher than the experimental value (1.40 D) and its direction is slightly different (α 104.7°) from that obtained in the calculations with the σ–π approximation (α 85.1°).[1b] However, both the phenyl rotation and a different conformation of the *N*-methyl group are energetically disfavoured and increase the dipole moment giving a larger disagreement with the experimental value.

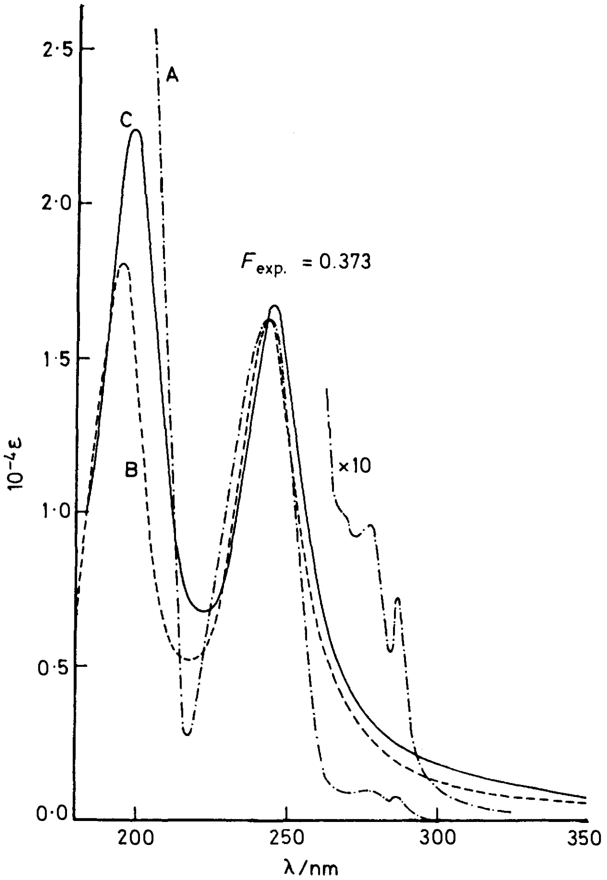
It is possible from the results of P and CNDO/CI calculations to identify an n–π* transition at 270 and 305 nm, respectively; a low intensity π–π* transition localized on the benzene ring at 266 and 271 nm; a charge-transfer π–π* transition from benzene ring to C=N group at 243 and 245 nm. The above results allow a fair simulation of the experimental electronic spectrum (Figure). It is noteworthy that the low intensity $(n–\pi^*)_1$ and $(\pi–\pi^*)_1$ transitions in the calculated absorption curve are covered by the tail of the most intense $(\pi–\pi^*)_2$ transition; however, the energy of the two transitions justifies the shape of the experimental curve. For the benzylideneamine, similar conclusions have been obtained by *ab initio* calculations with different basis sets for the planar conformation [11] and for the electronic structure of the lowest excited states.[12]

It is also interesting to point out that the weak bathochromic shifts observed for the π–π* bands (see Table 2) passing from non-polar to polar solvents are justified by the low values of the parameter C in the term dependent on the dielectric constant of the solvent.[13] The values obtained from P calculations for the compound (1) are given in Table 5.

TABLE 5

Transition	$(\pi-\pi^*)_1$	$(\pi-\pi^*)_2$
ΔE/eV	4.665	5.105
$(\mu_\pi)_e$	$2.48i + 1.06j$	$2.18i + 1.22j$
μ_e	$1.77i + 1.56j$	$1.47i + 1.72j$
$(\mu_e - \mu_g)\mu_g$	0.42	0.61
C/cm^{-1}	133	194

The *Z*-configuration of the derivative (1) cannot be planar. The minimum energy conformation obtained by the CNDO/2 method at θ 60° has an energy larger by 3.4 kcal mol^{-1} and a dipole moment higher (2.11 D) than those of the *E*-isomer. From the calculations, an ipsochromic shift is expected for the first three transitions of the electronic spectrum (see Table 4); such a shift is especially remarkable for the $(\pi-\pi^*)_2$ transition (from 243 to 218 nm) where a decrease in the intensity of the band should be expected. Direct comparison with experimental data is not possible because the *Z*-isomer was not obtained, neither as a pure compound nor in mixtures. In a future paper, other compounds will be considered as models for the *Z*-configuration.



Absorption curves for benzylidenemethylamine (1): experimental, A, in cyclohexane; and simulated, B, P method, C, CNDO/CI method

The coplanar *E*-configuration is also confirmed for compound (2) where steric hindrance is not different from that of derivative (1). P and CNDO/CI calculations give, respectively, for the $(n-\pi^*)_1$ transition, 269 and 302 nm; for the $(\pi-\pi^*)_1$ transition localized on the benzene ring, 268 and 279 nm; for the charge-transfer $(\pi-\pi^*)_2$ transition, 249 and 257 nm. The bathochromic shift of the charge-transfer band caused by the *p*-methyl is slightly underestimated by the P method and slightly overestimated by the CNDO/CI method with respect to the experimental value (8 nm in cyclohexane); this value is comparable with that observed for benzaldehyde.

In the imine (3), the *E*-configuration with θ 180° is energetically favoured by 2.4 kcal mol^{-1} relative to that with θ 0°. The conformational assignment by dipole moment analysis [1a] suggests a mixture of the two forms in the ratio 55 : 45. The dipole moment calculated for this mixture by the CNDO/2 method is 1.79 D; this value is larger than the experimental one (1.43 D), in agreement with the results found for the imine (1). The interconversion barrier between the two forms amounts to *ca.* 7 kcal mol^{-1} and prevents thermodynamic equilibrium. The differences in the electronic spectra calculated for the two forms by both P and CNDO/CI methods are not so great that the conformational assignment can be confirmed. The $(n-\pi^*)_1$ transition is calculated at 269 nm (P method) and 317 nm (CNDO/CI method), the localized $(\pi-\pi^*)_1$ transition at 273 (P) and 277 nm (CNDO/CI), the charge-transfer $(\pi-\pi^*)_2$ transition at 246 and 244 nm, respectively. The bathochromic shift due to the *o*-methyl is remarkably lower than that calculated for the *p*-methyl derivative and an intensity decrease is found both in the experimental and in the simulated spectrum.

In the compound (4), the conformational assignment is the same as for the imine (3). The usual transitions are calculated at 268, 274, and 252 nm for the P method and at 319, 283, and 257 nm for the CNDO/CI method. The bathochromic shift of the charge-transfer band caused by the *p*-methyl is again underestimated and overestimated by the P and CNDO/CI methods, respectively.

For compound (5), an n.m.r. study revealed the presence of the *E*- and *Z*-isomers in the ratio 93 : 7.[4] As the dipole moment of the parent 2,6-dimethylbenzylidenemethylamine is not available, the dipole moment analysis reported in ref. 1 is not possible. However, it can be supposed that the *E*-isomer is planar (θ 0°); in fact, on the R^2 side, steric hindrance is comparable with that of the planar *E*-isomer of α-methylbenzylidenemethylamine.[1a] On the other hand, the steric hindrance on the R^1 side is comparable with that of the most stable conformation (θ 180°) of the *E*-isomer of imine (3); this isomer too is planar. In the *Z*-isomer, the steric hindrance between R^1 and the *N*-methyl group is higher than that of the *Z*-isomer of α-methylbenzylidenemethylamine and, as a consequence, a θ value between 40 and 90° is expected. With this hypothesis, values of the dipole moment for the 2,6-dimethyl derivative may be calculated. By using the previously reported technique [1a] the calculated values have little dependence on the rotation angle θ of the *Z*-isomer (1.491 D at θ 40°;

1.495 D at θ 60°; 1.498 D at θ 80°). Also the simulated spectrum for a mixture of the planar *E*-isomer and of non-planar *Z*-isomers of the imine (5) in 93 : 7 ratio is nearly independent of the rotation angle of the *Z*-isomer. Therefore, we cannot obtain any reliable information on the conformation of the *Z*-isomer of this compound.

In a future paper, derivatives of α-methylbenzylidenemethylamine will be considered.

Financial support from the Italian C.N.R. is acknowledged.

[9/1105 *Received* 16*th July* 1979]

REFERENCES

[1] (*a*) Part 5, D. Pitea, G. Favini, and G. Capietti, *J.C.S. Perkin II*, 1977, 2038; (*b*) D. Pitea, D. Grasso, and G. Favini, *J. Chem. Soc.* (*B*), 1971, 2290.

[2] H. Suzuki, ' Electronic Absorption Spectra and Geometry of Organic Molecules,' Academic Press, New York, 1967.

[3] (*a*) T. Kubota, M. Yamakawa, and Y. Mori, *Bull. Chem. Soc. Japan*, 1963, **36**, 155; (*b*) M. El-Aasser, F. Abdel-Halim, and M. Ashraf El-Bayoumi, *J. Amer. Chem. Soc.*, 1971, **93**, 590; (*c*) D. Pitea, D. Grasso, and G. Favini, *J. Mol. Structure*, 1971, **10**, 101.

[4] J. Bjørgo, D. R. Boyd, C. G. Watson, W. B. Jennings, and D. M. Jerina, *J.C.S. Perkin II*, 1974, 1081.

[5] A. I. Vogel, ' Practical Organic Chemistry,' Longmans, London, 1959.

[6] D. Pitea and D. Grasso, *Spectrochim. Acta*, 1971, **27A**, 939.

[7] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, S129, S136.

[8] (*a*) J. Del Bene and H. H. Jaffè, *J. Chem. Phys.*, 1968, **48**, 1807; (*b*) R. L. Ellis, G. Kuehnlenz, and H. H. Jaffè, *Theor. Chim. Acta*, 1972, **26**, 131.

[9] J. A. Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375.

[10] N. Mataga and K. Nishimoto, *Z. Phys. Chem.* (*Frankfurt*), 1957, **13**, 140.

[11] G. Leroy, G. Louterman-Leloup, and B. Scheuer-Lamalle, personal communication.

[12] R. Cimiraglia and J. Tomasi, *J. Amer. Chem. Soc.*, 1977, **99**, 1135.

[13] G. Favini, D. Pitea, and F. Zuccarello, *Z. Phys. Chem.* (*Frankfurt*), 1973, **84**, 306.