ELSEVIER

Journal of Photochemistry and Photobiology
A: Chemistry 87 (1995) 203–207

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

Interaction of the ground and excited singlet states of 1,5- and 2,3-dimethoxynaphthalenes with some π-acceptors

Maged A. El-Kemary

Chemistry Department, Faculty of Education, Tanta University, Kafr ElSheikh, Egypt

Received 6 July 1994; accepted 15 November 1994

Abstract

1,5-Dimethoxynaphthalene (1,5-DMN) and 2,3-DMN were synthesized using the phase transfer catalysis (PTC) technique. Their fluorescence is quenched by 7,7,8,8-tetracyanoquinonedimethane (TCNQ), picric acid, chloranil and bromanil. The quenching rate constant values k_q were estimated. It was found that the rate of quenching of 2,3-DMN is slower than that of 1,5-DMN by the same acceptors. The role of the solvent polarity on the efficiency of fluorescence quenching of 1,5-DMN with picric acid was also studied. Spectral studies show that 2,3-DMN forms 1 : 1 charge transfer complexes (CTCs) with different π-acceptors in dichloromethane, while 1,5-DMN forms contact CTCs with TCNQ, chloranil and bromanil and 1 : 1 CTCs with tetracyanoethylene (TCNE) and picric acid. The equilibrium constants and thermodynamic standard reaction quantities of the CTCs were estimated.

Keywords: Excited state; Fluorescence; Dimethoxynaphthalenes; π-Acceptors; Charge transfer; Contact charge transfer

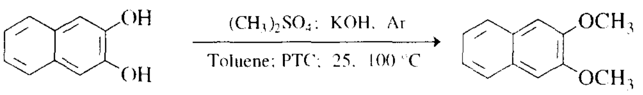
1. Introduction

Several groups have studied the quenching of the electronically excited states of dimethoxynaphthalenes (DMNs) with quenchers having no low-lying singlet states [1–4]. The role of charge transfer in the quenching process is still disputed. McCall et al. [5] have suggested that charge transfer is the dominant pathway in the quenching of 2,6-DMN by methylchloroacetate and 2-chloroacetamide. Recently, El-Kemary et al. [6] have suggested the importance of other electronic contributions to binding, in addition to charge transfer, in the quenching of 2,6-DMN by a series of π-acceptors. A similar effect is observed for the quenching of naphthalene fluorescence by conjugated dienes [1]. However, no investigations of the corresponding 1,5-DMN–π-acceptor systems have been performed.

In this paper, the fluorescence quenching of 2,3-DMN and 1,5-DMN using π-acceptors is presented. The ground state charge transfer complexes (CTCs) were studied spectrophotometrically. The association constant (K_4) and the molar absorption coefficient (ϵ_4) of the complexes at different temperatures were also determined using the Scott method [7].

2. Experimental details

2,3-DMN was prepared by the methylation of 2,3-dihydroxynaphthalene (2,3-DHN) in an Ar atmosphere using the phase transfer catalysis (PTC) technique according to the reaction scheme shown below.



A mixture of 16.1 g (0.1 mol) of 2,3-DHN (Aldrich) dissolved in 300 ml of freshly distilled toluene and 6.8 g (0.02 mol) of tetrabutylammonium hydroxide dissolved in 70 ml of water was stirred at 25 °C. The reaction was carried out under an Ar atmosphere (99.996%) in order to prevent auto-oxidation of the diphenols. To the reaction mixture, 25.2 g (0.2 mol) of dimethylsulphate was added at 12 °C (using an ice–H_2O bath) and stirring was continued for 2 h at room temperature; this was followed by refluxing at 100 °C for 2 h, after which the reaction mixture was allowed to cool. After cooling, 10 ml of 2 N NaOH and 20 ml of water were added and the reaction mixture was stirred for another 30 min. Then the toluene and combined toluene phases were washed with 2 N NaOH

SSDI 1010-6030(94)04004-4

and water. After drying over sodium sulphate, the solvent was evaporated in vacuum.

2,3-DMN was purified by recrystallization from benzene and vacuum sublimation (0.01 mmHg; bath temperature, 100 °C): melting point (m.p.), 119–120 °C (117 °C [8]); yield, 11.5 g (77%). The purity was tested by thin layer chromatography (TLC): stationary phase, silica (Merck); mobile phase, $CHCl_3$ (distilled).

1,5-DMN was prepared by the same PTC technique, starting from 1,5-DHN (Aldrich). 1,5-DMN was purified by recrystallization from ethanol, liquid chromatography (LC) (stationary phase, alumina; mobile phase, toluene and benzene–toluene (50 : 50)) and macrosublimation (0.01 mmHg; bath temperature, 100 °C): m.p., 179–180 °C (181–182 °C [8]; 181 °C [9]); yield, 96% (55% [10]).

Tetracyanoethylene (TCNE) (Aldrich) was recrystallized twice from chlorobenzene and sublimated three times in vacuum (m.p., 199–200 °C). 7,7,8,8-tetracyanoquinonedimethane (TCNQ) (Aldrich) was purified by sublimation. Chloranil and bromanil (Aldrich) were recrystallized from benzene. Picric acid (BDH) and dichloromethane (99.6% spectrophotometric grade) (Aldrich) were used without further purification.

Absorption spectra were recorded at various temperatures on a Shimadzu UV-240 spectrophotometer using 1 cm matched silica cells. The temperature was controlled to within ± 0.05 °C. All the evaluated data were measured with a sufficiently small error in the extinction interval $0.3 \leqslant E \leqslant 1.5$. The fluorescence intensities were recorded on a Shimadzu RF 540 spectrofluorometer, using excitation wavelengths of 325 nm and 310 nm for 1,5-DMN and 2,3-DMN respectively.

3. Results and discussion

The fluorescence of both 1,5-DMN and 2,3-DMN was efficiently quenched by the addition of various concentrations of π-acceptors, such as TCNQ, chloranil, bromanil and picric acid, in dichloromethane. The unquenched portion of the fluorescence had the same spectral distribution as that in solution without quencher. No new emission was detected in CH_2Cl_2. Stern–Volmer plots were constructed from the relative integrated fluorescence intensities, and the Stern–Volmer quenching coefficients K_{sv} were obtained using the method of linear regression according to the relation [11]

$$I_0/I = 1 + K_{sv}[Q] = 1 + k_q \tau_0[Q] \qquad (1)$$

where I_0 and I are the relative fluorescence intensities in the absence and presence of quencher with concentration [Q], and τ_0 is the fluorescence lifetime of the fluorophore in the absence of quencher. The fluorescence lifetimes of 1,5-DMN and 2,3-DMN were 10.08 ns [12] and 16.8 ns [4] respectively. The experimental results are presented in Table 1, where the Stern–Volmer quenching coefficients K_{sv}, bimolecular quenching rate constants k_q and correlation coefficients r are given. Typical Stern–Volmer plots are shown in Figs. 1 and 2.

At high quenching concentration, Stern–Volmer plots show deviations from linearity (Fig. 2). This behaviour is probably due to the absorption of incident light by the ground state CTC between the fluorophore and the quencher. Hence, in these cases, k_q values were estimated with low [Q] to minimize ground state complex formation.

Table 1 shows the rate constants k_q for quenching of 1,5-DMN and 2,3-DMN fluorescence by a number of π-acceptors. The quenching efficiency (magnitude of k_q) appears to be dependent on the electron affinity of the quencher. However, no general trends were observed. This behaviour may conceivably be due to uncontrolled steric factors, but probably indicates the importance of other contributions to binding in addition to charge transfer from the fluorophore to the π-acceptor [1].

On the other hand, the position of the methoxy group on the aromatic ring may play a crucial role in the efficiency of quenching of the fluorescence of DMNs by π-acceptors. The methoxy group is an electron donor and, on the whole, it increases the electron density on the aromatic ring [13]. It is also known that an increase in the number of electron substituents leads to an increase in the basicity of the aromatic ring [14]. In this case, when the basicity of the aromatic ring is increased and the degree of charge transfer from the substituent to the ring is increased, the effectiveness of quenching should increase. Interestingly, the rate of quenching of 2,3-DMN is slower than that of 1,5-DMN by the same acceptors; this can be attributed to the steric hindrance caused by the adjacent methoxy groups in the 2 and 3 positions, and therefore the degree of charge transfer from the substituent to the ring should be less for 2,3-DMN than for 1,5-DMN.

The quenching rate constants are dependent on the solvent polarity. The results show that the rate of quenching of 1,5-DMN using picric acid is slower in hexane (23.74×10^{11} s^{-1} M^{-1}) than in dichloromethane (34.49×10^{11} s^{-1} M^{-1}). This may be due to a polar medium effect. A similar behaviour was also observed by McCall et al. [2] for the quenching of 2,6-DMN by methylchloroacetate, and by El-Kemary et al. [6] for the quenching of 2,6-DMN by π-acceptors, but not by Solomon et al. [15] for the quenching of the fluorescence of aromatic hydrocarbons by quadricyclene. Also, in hexane and dichloromethane, the k_q values of 1,5-DMN with picric acid are much larger than the limiting diffusion rate constant k_{diff}. The calculated k_{diff} values are 1.89×10^9 l mol^{-1} s^{-1} in hexane and 1.27×10^8 l mol^{-1} s^{-1} in dichloromethane [16]. This indicates that diffusion is not involved in the quenching mechanism.

Table 1
Fluorescence quenching data obtained at room temperature in CH_2Cl_2

Fluorophore	Quencher	$k_q\tau_0$ (m^{-1})	k_q (s^{-1} m^{-1})	r
1,5-DMN	TCNQ	26903.52 ± 197	$(26.69 \pm 1.95) \times 10^{11}$	0.989
1,5-DMN	Bromanil	15543.36 ± 262	$(15.42 \pm 1.5) \times 10^{11}$	0.998
1,5-DMN	Picric acid	34765.92 ± 312	$(34.49 \pm 3.4) \times 10^{11}$	0.980
1,5-DMN	Chloranil	842.48 ± 81.5	$(8.358 \pm 0.8) \times 10^{10}$	0.973
2,3-DMN	TCNQ	11392.0 ± 54	$(67.81 \pm 3.2) \times 10^{10}$	0.995
2,3-DMN	Picric acid	1841.26 ± 33	$(10.96 \pm 1.96) \times 10^{10}$	0.970
2,3-DMN	Chloranil	1215.98 ± 28	$(7.238 \pm 1.66) \times 10^{10}$	0.999

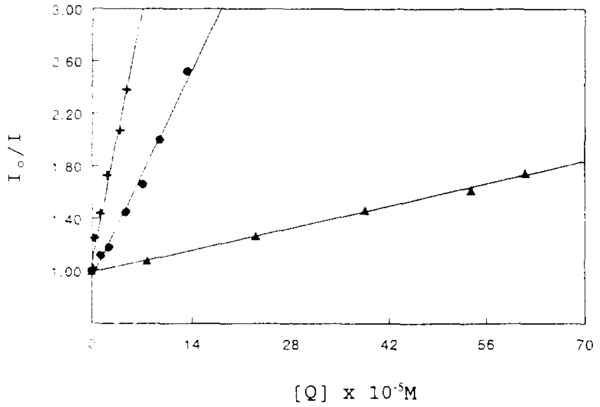


Fig. 1. Stern–Volmer plots for the quenching of the fluorescence of 1,5-DMN by TCNQ (+) and of 2,3-DMN by TCNQ (●) and chloranil (▲) in dichloromethane.

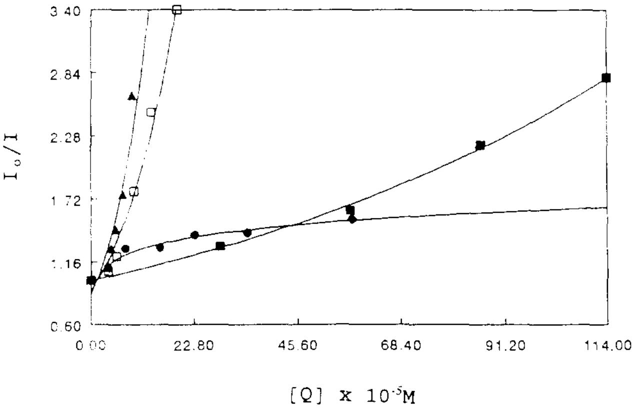


Fig. 2. Stern–Volmer plots for the quenching of the fluorescence of 1,5-DMN by picric acid (▲), chloranil (●) and bromanil (□) and of 2,3-DMN by picric acid (■) in dichloromethane.

Table 2
Maximum absorption wavelengths (λ_{max}), equilibrium constants (K_4), molar absorption coefficients (ϵ_4) and correlation coefficients (r) for 1,5-DMN and 2,3-DMN with various π-acceptors at different temperatures

Temperature (°C)	λ_{max} (25 °C) (nm)	K_4 (l mol^{-1})	ϵ_4 (l mol^{-1} cm^{-1})	r
1,5-DMN–TCNE				
10.00		24.31	1889.86	0.971
18.00		20.94	1901.43	0.976
25.000	420, 772	18.17	1920.55	0.983
31.00		17.68	1897.37	0.981
1,5-DMN–Picric acid				
10.00		11.14	550.23	0.981
18.00		9.84	562.55	0.991
25.00	448	8.01	559.47	0.993
31.00		6.84	569.52	0.982
2,3-DMN–TCNQ				
10.00		15.22	226.20	0.980
18.00		13.71	233.01	0.984
25.00	596	12.42	220.72	0.987
31.00		10.57	231.47	0.972
2,3-DMN–TCNE				
10.00		13.89	3274.93	0.973
18.00		12.54	3159.62	0.980
25.00	591	11.22	3301.78	0.981
31.00		10.14	2367.15	0.978
2,3-DMN–Chloranil				
10.00		5.15	972.34	0.971
18.00		4.81	989.46	0.986
25.00	525	4.41	961.63	0.980
31.00		3.07	984.64	0.977

Table 2 lists the absorption maxima (λ_{max}, nm), equilibrium constants (K_4, l mol^{-1}) and molar absorption coefficients (ϵ_4, l mol^{-1} cm^{-1}) at λ_{max} of the CTCs of 2,3-DMN and 1,5-DMN with TCNE, TCNQ, chloranil and picric acid in dichloromethane at various temperatures.

The charge transfer spectra of the complexes of 2,3-DMN with different π-acceptors show only one absorption band in the visible region, characteristic of an intermolecular charge transfer band. The absorption spectra of the CTCs of 1,5-DMN show two absorption bands with TCNE and only one absorption band with the other acceptors investigated.

A study of the evaluated data was performed to determine whether the multiplicity of the charge transfer band of the 1,5-DMN–TCNE system was due to the presence of different isomeric complexes or an additional termolecular complex. As shown in Fig. 3, the electronic absorption spectra of the 1,5-DMN–TCNE complex has two charge transfer bands. The relative intensities of these two bands do not vary with tem-

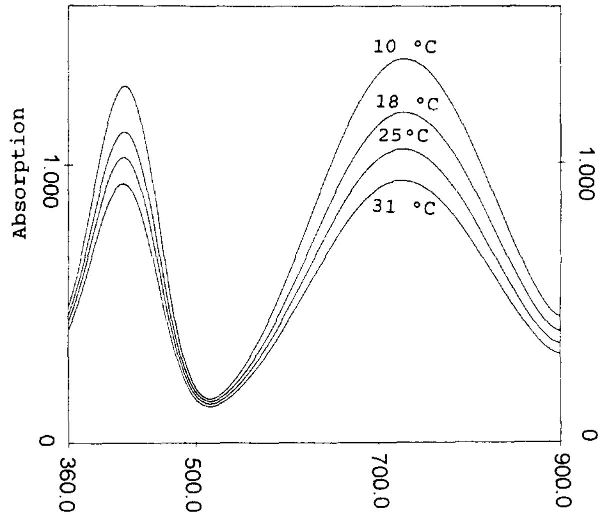


Fig. 3. Charge transfer spectra of 1,5-DMN and TCNE at different temperatures.

perature within the range 283–304 K. Thus the bands are not associated with the presence of two 1 : 1 isomeric structures. Also, it was found that a linear regression according to the Scott relation [7] for the estimation of K_4 and ϵ_4 leads to a good linear representation with a correlation coefficient of 0.97 or greater. Hence, only one complex is formed for this system. More importantly, using multiwavelength linear regression of concentration-dependent absorbance data [17], no evidence is found of significant concentrations of 2 : 1 (D_2A) complexes. Therefore the band multiplicity may arise from a wide range of energetically accessible conformations [18] of the 1,5-DMN–TCNE complex involving the overlap of the lowest unoccupied molecular orbital (LUMO) of the acceptor with either the highest occupied molecular orbital (HOMO) or HOMO − 1 of 1,5-DMN.

The values of ϵ_4 collected in Table 2 vary with temperature, but only by a very small amount (about 3%). This deviation is small compared with the usual error in the absorption measurements. Therefore it is recognized that the calculated values of ϵ_4 at different temperatures are equal, with deviations expected from the error in the absorption measurements. The approximate constancy of the ϵ_4 values may be taken as further evidence for the existence of only a 1 : 1 CTC [19].

Linear regression on the basis of the Scott relation of 1,5-DMN–TCNQ, 1,5-DMN–chloranil and 1,5-DMN–bromanil systems yields lines with negative slopes, indicating that the interaction of 1,5-DMN with TCNQ or chloranil orbitals is extremely weak and that the spectra are due to contact charge transfer (CCT) interactions [19].

The determination of K_4 and ϵ_4 for the 2,3-DMN–picric acid system was impossible, because of the strong overlap of the charge transfer band with the acceptor band.

Analysis of the data in Table 2 indicates that the K_4 values of 1,5-DMN–TCNE complexes are about twofold larger than those obtained for the corresponding 2,3-DMN–TCNE complexes. This may be attributed to the steric hindrance of complex formation due to the adjacent methoxy groups in the 2 and 3 positions in 2,3-DMN.

The thermodynamic standard reaction quantities ($\Delta G°$, $\Delta H°$ and $\Delta S°$) were estimated from the temperature dependence of the equilibrium constant K_4 [20]. There is no evidence of deviation from linearity for the plot of $\ln K_4$ vs. $1/T$ over the investigated temperature range for the systems studied. This is not surprising due to the assumed 1 : 1 complex for the systems. The estimated values given in Table 3 indicate that the enthalpies of formation ($-\Delta H°$) for 2,3-DMN complexes increase slightly with increasing electron affinity of the acceptors, accompanied by parallel increases in $-\Delta G°$ and $-\Delta S°$. There is an approximate linear relationship between $-\Delta G°$ and $-\Delta S°$ (Fig. 4). This implies that the free energy or entropy on formation of the complex increases due to the more restricted configuration of the atoms as the complex becomes more stable [21]. It has been shown that the contribution to the entropy of formation comes mainly from the energy of the electron donor–acceptor interaction, with

Table 3
Thermodynamic standard reaction quantities of 1,5-DMN and 2,3-DMN with various π-acceptors

System	$-\Delta H°$ (kJ mol^{-1})	$-\Delta S°$ (J mol^{-1} K^{-1})	$-\Delta G°$ (kJ mol^{-1})
1,5-DMN–TCNE	11.43 ± 1.49	13.97 ± 4.98	7.33 ± 0.18
1,5-DMN–Picric acid	16.90 ± 1.91	39.44 ± 6.56	5.30 ± 0.15
2,3-DMN–TCNQ	11.98 ± 1.66	19.54 ± 5.65	6.09 ± 0.09
2,3-DMN–TCNE	10.58 ± 0.64	15.41 ± 2.19	5.91 ± 0.20
2,3-DMN–Chloranil	8.16 ± 0.86	15.11 ± 2.95	3.72 ± 0.15

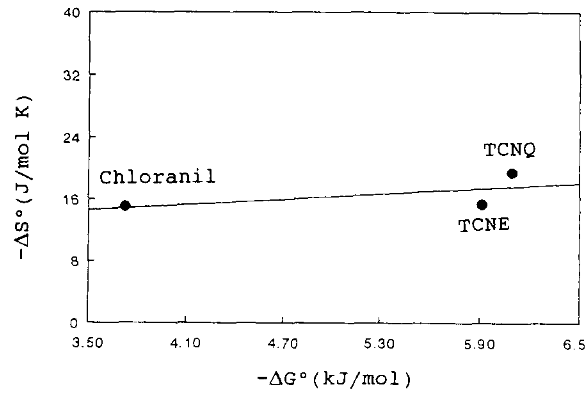


Fig. 4. Relationship between $-\Delta S°$ and $-\Delta G°$ for CTCs of 2,3-DMN.

a small contribution from the changes in translational, rotational and vibrational energy levels of the reactants on complex formation [22]. As can be inferred from the data, the values of $-\Delta H°$ and $-\Delta G°$ for 1,5-DMN–TCNE are slightly larger than for the 2,3-DMN–TCNE complex due to the steric hindrance of complex formation by the adjacent methoxy groups in the 2 and 3 positions in 2,3-DMN.

The charge transfer energy (ΔE_{CT}) of the lowest intermolecular charge transfer band is related to the electron affinity (E^A) of the acceptors with a certain donor by the expression [23]

$$\Delta E_{CT} = I_p - E^A - W \tag{2}$$

where W is the dissociation energy of the charge transfer excited state. The value of the ionization potential (I_p) of the donors was obtained from the empirical linear relationship between I_p and ν_{CT} [23]

$$I_p = 5.21 + 1.65 \times 10^{-4} \nu_{CT} \text{ (TCNE)} \tag{3}$$

where ν_{CT} is the wavenumber in reciprocal centimetres of the first charge transfer band formed between the donor and the acceptor TCNE in CH_2Cl_2. The values of I_p of 1,5-DMN and 2,3-DMN are 7.41 eV and 7.92 eV respectively. Unfortunately, the I_p values for the donors 1,5-DMN and 2,3-DMN are not available in the literature; therefore a comparison of the I_p values determined from the charge transfer energy with those obtained by other techniques is not possible. The energies (W) of the charge transfer excited state (Table 4) were estimated on the basis of relation (2) using the values of I_p of the donors calculated by relation (3).

Table 4
Absorption and dissociation energies (ΔE_{CT} and W) of the CTCs of 1,5-DMN and 2,3-DMN with different π-acceptors in dichloromethane and electron affinities (E^A) of the acceptors

System	E^A (eV)	ΔE_{CT} (eV)	W (eV)
1,5-DMN–TCNE	1.60 [24, 25]	1.61	4.21
1,5-DMN–Picric acid	1.45 [26]	2.33	3.64
2,3-DMN–TCNQ	1.70 [24, 25]	1.75	4.47
2,3-DMN–TCNE	1.60 [24, 25]	1.76	4.55
2,3-DMN–Chloranil	1.37 [24, 25]	1.98	4.57

Acknowledgments

Professor W. Liptay and Dr. N. Detzer (Institute of Physical Chemistry, Mainz University, Germany) are gratefully acknowledged for their help in the synthesis of the compounds.

References

[1] D.A. Labianca, G.N. Taylor and G.S. Hammond, *J. Am. Chem Soc., 94* (1972) 3679.
[2] M.T. McCall, G.S. Hammond, O. Yonemitsu and B. Witkop, *J. Am. Chem. Soc., 93* (1971) 2081.
[3] F.H. Quina, Z. Hamlet and F.A. Carroll, *J. Am. Chem. Soc., 98* (1976) 2240.
[4] P.C. Wong and D.R. Arnold, *Can. J. Chem., 58* (1980) 918.
[5] M.T. McCall, G.S. Hammond, O. Yonemits and B. Witkop, *J. Am. Chem. Soc., 92* (1970) 6991.
[6] M. El-Kemary, A.M. Ibrahim and S.H. Etaiw, *Can. J. Appl. Spectrosc.,* accepted for publication.
[7] R.L. Scott, *Rec. Trav. Chim., 75* (1956) 787.
[8] A.J. Birch and P. Hextall, *Aust. J. Chem., 6* (1954) 263.
[9] K.B. Everad and L.E. Sutton, *J. Chem. Soc.,* (1949) 2312.
[10] M. Charles and H.J. Gardner, *J. Am. Chem. Soc., 53* (1931) 4109.
[11] O. Stern and M. Volmer, *Phys. Z., 20* (1919) 183.
[12] S.I. Druzhinin, L.K. Zhubanoua and B.M. Uzhinov, *Dokl. Akad. Nauk SSSR, 279* (3) (1984) 669.
[13] O.A. Reutov, *Theoretical Bases of Organic Chemistry*, Izd, MGU, Moscow, 1964 (in Russian).
[14] N. Mataga, *Bull. Chem. Soc. Jpn., 36* (9) (1963) 1109.
[15] B.S. Solomon, C. Steel and A. Weller, *Chem. Commun.,* (1969) 927.
[16] J.G. Calvert and J.N. Pitts, Jr., *Photochemistry*, Wiley, New York, 1967, p. 627.
[17] T.D. Russell and D.H. Levy, *J. Phys. Chem., 89* (1982) 2718.
[18] R.S. Mulliken and W.B. Berson, *Molecular Complexes*, Wiley, New York, 1969.
[19] R.S. Mulliken, *J. Chim. Phys., 61* (1964) 20.
[20] K.S. Pitzer and L. Brewer, *Thermodynamics*, McGraw-Hill, New York, 2nd edn., 1961.
[21] S.C. Liao and R.K. Chan, *Can. J. Chem., 49* (1971) 2700.
[22] W.B. Person, *J. Am. Chem. Soc., 84* (1962) 536.
[23] H.M. McConnel, J.S. Ham and J.R. Platt, *J. Chem. Phys., 21* (1964) 66
[24] G. Briegleb, *Angew. Chem., 8* (1964) 326.
[25] G. Briegleb and J. Czekalla, *Z. Elektrochem., 63* (1959) 6.
[26] R.M. Ramadan, A.M. El-Atrsh and A.M. Ibrahim, *Spectrochim. Acta, Part A, 46* (1990) 1305.