



Charge–transfer complexes of pyrimidine Schiff bases with aromatic nitro compounds

Yousry M. Issa*, A.L. El Ansary, O.E. Sherif, H.B. Hassib

Chemistry Department, Faculty of Science, Cairo University, Gamaa Street, Giza, Egypt

ARTICLE INFO

Article history:

Received 8 July 2010

Received in revised form 21 February 2011

Accepted 11 March 2011

Keywords:

Charge–transfer complexes

Pyrimidine Schiff bases

Spectroscopy

Donor–acceptor interaction

Molecular complexes

ABSTRACT

Charge–transfer (CT) complexes of pyrimidine Schiff bases, derived from condensation of 2-aminopyrimidine and substituted benzaldehydes, with some aromatic polynitro compounds were prepared and investigated using IR, UV, visible and ^1H NMR spectroscopy. For all solid complexes, the main interaction between the donor and acceptor molecules takes place through the π – π^* interaction. Strong and some weak acidic acceptors, in addition interact through proton transfer from the acceptor molecule to the basic centre of the electron donor. Also, an n – π^* transition was detected in some complexes.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Schiff bases attracted the attention of many researchers due to their wide applications and importance, as corrosion inhibitors [1], catalyst carriers [2,3], thermo-stable materials [4–6], metal ion complexing agents [7] and in biological systems [8,9].

Recently, Schiff-base model compounds with different central groups and various side-group substitutions have been synthesized and characterized by elemental analysis, DSC technique, ^1H NMR, FTIR and UV–vis spectroscopy measurements [10].

Several investigations have been made concerning the charge–transfer complexes of aromatic nitro compounds with various aromatic donor compounds [11–15]. Such studies were devoted to evaluate the ionization potential of donor, or electron affinities of acceptors as well as the importance of π – π^* bonding in complex formation. Few studies are concerned with CT complexes of Schiff bases [16,17]. Hindawey et al. [18] investigated the solid complexes of *p*-nitrophenol as well as some dinitro and trinitrobenzenes with *p*-substituted benzylidenaniline. The molecular complexes of some hydroxy Schiff bases with polynitrobenzenes were studied [19].

Molecular complexes of the donor–acceptor type formed between aromatic amines and π -acceptors were the subject of extensive studies [20–22]. Recently, *N*-heterocyclic compounds, were used as efficient donors in the preparation of CT complexes with different *p*-benzoquinone derivatives [23,24].

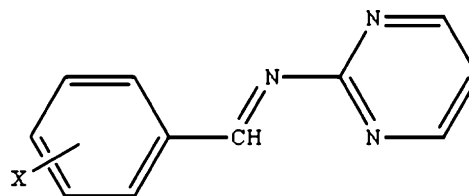
The present study deals with the preparation of charge–transfer complexes of some pyrimidine Schiff bases with di- and tri-nitrobenzene derivatives. They were investigated using IR, UV–visible and ^1H NMR spectroscopy to identify the type of bonding between the donor and acceptor molecules in the CT complexes.

2. Experimental

All chemicals used in this investigation were pure laboratory grade BDH (England) and Fluka chemicals. The aminopyrimidine Schiff bases used were prepared by condensation of equimolecular amounts of 2-aminopyrimidine and the corresponding aldehydes. The products were recrystallized from ethanol till constant m.p. [25]. The prepared Schiff bases have the following formulae (Scheme 1).

Where $x = \text{H}$ (a), *o*-OH (b), *p*-OH (c), *p*-OCH₃ (d), *o*-NO₂ (e), *p*-NO₂ (f), *p*-Cl (g), *m*-Cl (h), *p*-Br (i), *p*-N(CH₃)₂ (j) and *o*-OH (Naph.) (k).

The acceptors used are picric acid (1), 3,5-dinitrosalicylic acid (2), 3,5-dinitrobenzoic acid (3), 2,4-, 2,5- and 2,6-dinitrophenols



Scheme 1. Structural formula of pyrimidine Schiff bases.

* Corresponding author. Tel.: +20 2 35868094; fax: +20 2 35728843.

E-mail address: yousrymi@yahoo.com (Y.M. Issa).

(4, 5 and 6), p-nitrophenol (7), picryl chloride (8), trinitrobenzene (9), m-dinitrobenzene (10), 1-chloro-2,4-dinitrobenzene (11), 1-fluoro-2,4-dinitrobenzene (12) and 1,5-difluoro-2,4-dinitrobenzene (13).

2.1. Preparation of charge–transfer complexes

The CT, 1:1 and 1:2, complexes were prepared as described previously [26] by mixing a hot saturated ethanolic solution of the donor with an equivalent amount of the acceptor. The solid complexes were either separated immediately, e.g. picric acid, or on standing. The ethanol soluble complexes were recrystallized from ethanol while the insoluble complexes were just boiled with ethanol to ensure freeing from contaminations of unreacted products. The resulting products were subjected to elemental analysis in the Micro Analytical Centre, Faculty of Science, Cairo University. The obtained results were in high agreement with those theoretically calculated.

2.2. Apparatus

The IR spectra were obtained by using a PYE UNICAM SP 1000 infrared spectrometer as KBr discs. The electronic absorption spectra were recorded on a PYE UNICAM SP 1750 spectrophotometer using the Nujol mull technique to obtain the electronic absorption spectra of some charge–transfer complexes in the solid state as they dissociate in polar solvents. The ^1H NMR spectra were recorded using a VARIAN EM-390 (90 MHz) spectrometer using tetramethylsilane (TMS) as internal reference and Merck- d^6 dimethylsulphoxide (DMSO) as a solvent.

3. Results and discussion

3.1. Infrared spectral studies

The IR spectra of the complexes are studied and the main bands compared with their analogues in free donors [25] and acceptors. From these studies the type of interaction observed in these complexes is elucidated. For all studied complexes, it is noticeable that the γCH bands of the donor part are shifted to higher values while those of the acceptor are displaced in the opposite direction. This is a result of intermolecular π – π^* electron transfer from

the highest occupied π -level on the donor molecule (HOMO) to the lowest unoccupied level on the acceptor (LUMO). The hetero ring is the centre of charge–transfer as noticed from the observed shift to much lower values with respect to the benzal ring. A peculiar behavior is observed for the p-N-dimethyl derivative (j) as the benzal ring is the centre of electron donation.

Depending on the nature of the acceptor used, the charge–transfer complexes are classified into three groups.

3.1.1. Complexes with strong acidic acceptors

These include the CT complexes with acceptors (1), (2) and (3) in molar ratio 1:1. The 1:2 (D:A) complexes of some donors with picric acid were also studied. The main IR bands of some representative 1:1 and 1:2 complexes with picric acid are collected in Table 1. In this class of compounds, the acceptors exhibit acidic character while the donors reveal basic character. Thus, an acid–base interaction involving a proton transfer from the acceptor to the donor is to be expected. The basic centre or the proton acceptor would be the azomethine nitrogen in case of Schiff bases a–i and k, and the dimethylamino nitrogen in case of j. The proton transfer originates from the OH group of the acceptors (1) and (2) and the COOH group of (3). Such mechanism of proton transfer is deduced from the disappearance of the bands corresponding to these acidic centres observed at 3110, 3190 and 3570 cm^{-1} for the free acceptors in the spectra of the 1:1 CT complexes. Also the spectra display new broad intense bands within the wave number range 3300–2100 cm^{-1} which correspond to a proton linked to a positively charged nitrogen atom ($=^+\text{N-H}$) [27]. However, for the 1:2 complexes with picric acid, the $-\text{NH}$ bands are observed within the wave number range 3020–2360 cm^{-1} . This band is formed through the transfer of a proton from one of the two acceptor molecules to the basic centre of the donor. This is supported by the appearance of the νOH band of the second picric acid molecule at 3110 cm^{-1} [27]. It is noteworthy to mention that, for donor j with p-N(CH₃)₂ group on the benzal ring, the νOH band of the second picric acid molecule also disappears as a result of the existence of two acid–base interactions, the first with the N(CH₃)₂ and the second with the azomethine nitrogen.

The C=N band undergoes the same behavior in the case of 1:1 and 1:2 complexes. The $\nu\text{C=N}$ is shifted to higher values for most CT complexes except for donor j a counter shift is observed. This is attributed to the attachment of the proton in such case to the p-N(CH₃)₂ group and not to the azomethine nitrogen.

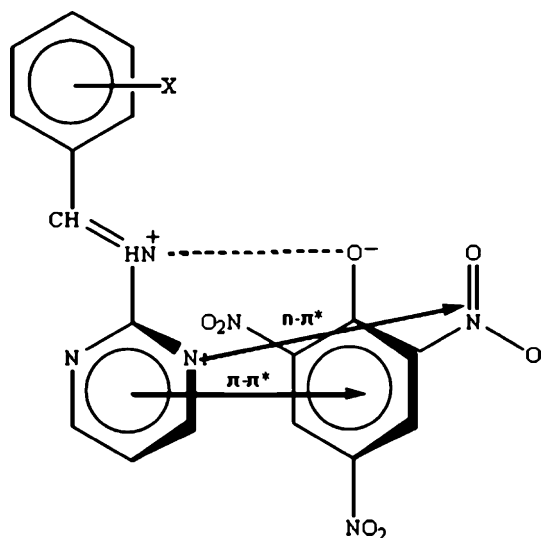
Table 1
Characteristic IR bands of charge–transfer complexes of pyrimidine Schiff bases with picric acid.

| No | X | Color | m.p. (°C) | NH ⁺ | (OH) | NO ₂ asym. | NO ₂ sym. | ⁸ CH _{acceptor} |
|------------------------|------------------------------------|-----------------|-----------|-----------------|-------|-----------------------|----------------------|-------------------------------------|
| Bands of free acceptor | | | | | | 1555,1540,1530 | 1350 | 784 |
| 1:1 (D:A) complexes | | | | | | | | |
| a | H | Canary yellow | 229 | 3940–2100 | | 1571,1550 | 1340,1330 | 745 |
| b | o-OH | Yellow | 215 | 3980–2600 | | 1570,1552 | 1338,1325 | 748 |
| c | p-OH | Yellow | >240 | 3000–2360 | | 1570,1552 | 1340,1330 | 748 |
| d | p-OCH ₃ | Lemon yellow | 198 | 3000–2600 | | 1575,1555,1540 | 1335,1335 | 747 |
| e | o-NO ₂ | Lemon yellow | 226 | 2940–2630 | | 1570,1550 | 1340,1327 | 747 |
| f | p-NO ₂ | Brownish yellow | 224 | 2940–2640 | | 1570,150,1583 | 1340,1338sh | 745 |
| g | p-Cl | Lemon yellow | 230 | 2930–2600 | | 1572,1552 | 2347,1330 | 745 |
| h | m-Cl | Yellow | 235 | 2900–2400 | | 1552 | 1325 | 745 |
| i | p-Br | Yellow | >240 | 3030–2480 | | 1572,1552 | 1340,1328 | 747 |
| j | p-N(CH ₃) ₂ | Orange yellow | 202 | 2940–2600 | | 1571,1550 | 1340,1328 | 747 |
| k | o-OH naph | Lemon yellow | 226 | 3000–2500 | | 1570,1540 | 1342,1332 | 742 |
| 1:2 (D:A) complexes | | | | | | | | |
| a | H | Lemon yellow | 220 | 3000–2360 | 3100 | 1578,1548,1522 | 1342 | 772 |
| b | o-OH | Canary yellow | 205 | 3000–2400 | 3095b | 1570,1560 | 1338,1328, | 747s |
| d | p-OCH ₃ | Canary yellow | 227 | 3020–2480 | 3100 | 1570,1550 | 1345,1550 | 745 |
| g | p-Cl | Yellow | 219 | 3000–2500 | 3100 | 1572,1550 | 1348,1325 | 745 |
| i | p-N(CH ₃) ₂ | Canary yellow | 163 | 3000–2360 | – | 1570,1549 | 1340,1330 | 745 |

sh = shoulder, s = strong, b = broad, w = weak.

Compd: (OH), (-OH), (C-OH).

b: 3140b 1280 1174w.



Scheme 2. Structure of 1:1 CT complex of picric acid with a–i and k Schiff bases.

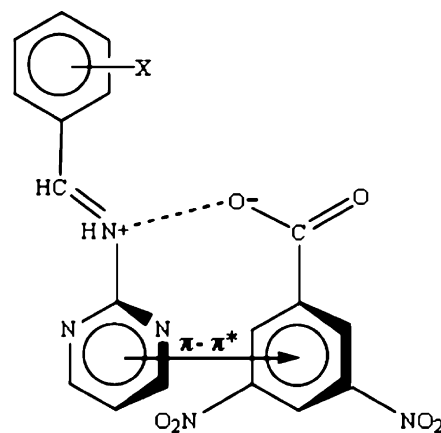
The $\nu_{\text{asym. NO}_2}$ bands of the acceptors display some interesting changes. The three bands in the spectrum of picric acid (1555, 1540 and 1530 cm^{-1}) are reduced to two bands in the complex. This is due to the rupture of the intramolecular hydrogen bond between the OH-group and the neighboring NO_2 group. One of these two asym. NO_2 bands, is shifted to lower wave number while, the second exhibits a counter shift. This is explained by invoking the participation of the two NO_2 groups in positions 2 and 6 in $n-\pi^*$ electronic interaction with the two nitrogen atoms of the pyrimidine ring. This interaction is allowed by the orientation of the picric acid ion to a position facilitating the formation of the electrostatic bond between the positive and negative centres resulting from proton transfer. In the case of dinitrosalicylic acid (1540 and 1530 cm^{-1}) the orientation of the molecule permits the participation of only one nitro group in $n-\pi^*$ electronic transition. The asym. NO_2 bands of 3,5-dinitrobenzoic acid (1555 and 1540 cm^{-1}) display shifts to lower wave numbers. This is attributed to an increased electron density on the acceptor molecules as a result of the $\pi-\pi^*$ interaction.

The $\nu_{\text{sym. NO}_2}$ bands are mostly shifted to lower wave numbers in accordance with the increased π -electron density on the ring of the acceptor molecule of the CT complexes.

Based on the above findings the charge–transfer complexes may be represented by the following formulae (Schemes 2–5).

3.1.2. Complexes with weak acidic acceptors

The main IR bands of some representative 1:1 complexes of the investigated Schiff bases with 2,4-, 2,5-, 2,6-dinitrophenols and p-nitrophenol (4–7) are collected in Tables 2 and 3. The 1:2 (D:A)



Scheme 3. Structure of 1:1 CT complex of 3,5-dinitrobenzoic acid with the investigated Schiff bases.

complexes of some representative Schiff bases with 2,4- and 2,6-dinitrophenols were prepared, Table 4.

The infrared spectra reveal that the complexes formed between the investigated donors and the weak acidic acceptors may involve, in some cases, proton transfer besides the $\pi-\pi^*$ electronic interaction.

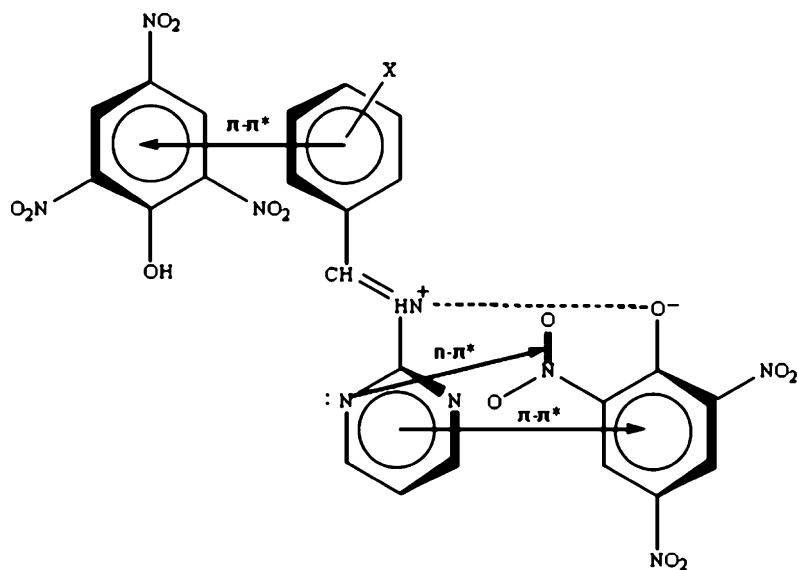
The molecular complexes of almost all investigated Schiff bases with acceptors 4, 5 and 7 exhibit new intense broad bands within the $3040\text{--}2200\text{ cm}^{-1}$ corresponding to $\text{N}^+\text{--H}$ stretching mode of a proton linked to quaternary positively charged nitrogen [17]. Meanwhile, the bands corresponding to the νOH of the free acceptors appearing at 3270 , 3270 and 3610 cm^{-1} , respectively are no more observed. This may be clarified by assuming the transfer of a proton from the acidic OH group of the acceptor to a basic centre on the donor molecule. Mention is to be made that complexes of both (e and f) with acceptors (4) and (7) and (e) with acceptor (6) do not show the NH^+ band. The incapability of these donors to exhibit proton transfer is due to the presence of the electron withdrawing nitro group which causes a decrease in the basicity of the nitrogen atoms. Further evidence of the above conclusion is the observed shift of the γCH band of the $\text{CH}=\text{N}$ linkage to lower wave number values in the case of complexes showing proton transfer, while in the other type of complexes, showing no proton transfer, a shift to higher values is observed. The latter is attributed to decreased electron density on the $\text{CH}=\text{N}$ centre as a result of complex formation.

On the other hand, the IR spectra of the complexes of 2,5-dinitrophenol with the exception of (j), denotes the absence of proton transfer. This is based on the appearance of the bands corresponding to the νOH in the spectra of the complexes. These bands show slight shifts to higher wave number indicating the destruction of the intramolecular hydrogen bonding between the OH and the neighboring nitro group in the free acceptor on complexation.

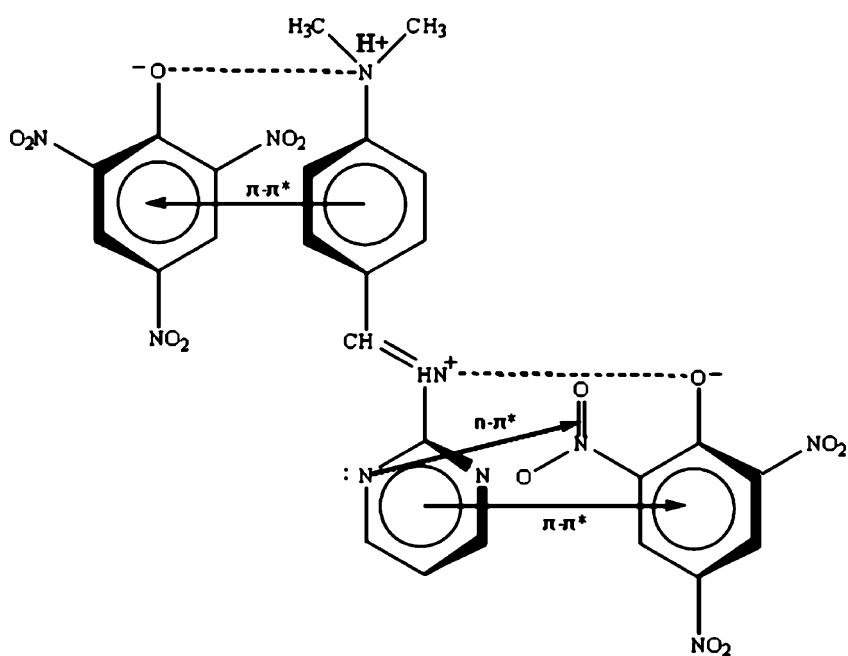
Table 2

Characteristic IR bands of charge–transfer complexes of pyrimidine Schiff bases with 2,4-dinitrophenol (1:1).

| No | Color | m.p. ($^{\circ}\text{C}$) | NH^+ | $\text{NO}_{2\text{asym.}}$ | $\text{NO}_{2\text{sym.}}$ | $^8\text{CH}_{\text{acceptor}}$ |
|------------------------|---------------|-----------------------------|---------------|-----------------------------|----------------------------|---------------------------------|
| Bands of free acceptor | | | | | | |
| a | Canary yellow | 132 | 2800–2200 | 1540,1540 | 1350 | 928,825 |
| b | Yellow | 124 | 2750–2305 | 1539,1530 | 1530 | 924,820 |
| c | Canary yellow | 104 | 2800–2300 | 1538 | 1345 | 925,793 |
| d | Canary yellow | 133 | 2810–2200 | 1540 | 1340 | 919,810 |
| e | Canary yellow | 133 | 2810–2200 | 1538 | 1342 | 925,825 |
| e | Brown | 102 | – | 1538 | 1350 | 925,795 |
| f | Light yellow | 79 | – | 1540 | 1350 | 928,790 |
| g | Canary yellow | 131 | 2700–2200 | 1540b | 1340 | 926,827 |
| h | Canary yellow | 126 | 2790–2200 | 1540b | 1345 | 925,– |
| i | Canary yellow | 130 | 2800–2200 | 1535 | 1342 | 925,970 |
| j | Orange | 123 | 2820–2200 | 1540 | 1345 | 925,825 |
| k | Brown | 83 | – | 1540 | 1335 | 924,822sh |



Scheme 4. Structure of 1:2 CT complex of picric acid with a-i and k Schiff bases.



Scheme 5. Structure of 1:2 CT complex of picric acid with Schiff base j.

Table 3
Characteristic IR bands of charge–transfer complexes of pyrimidine Schiff bases with p-nitrophenol (1:1).

| No | Color | m.p. (°C) | NH ⁺ | NO ₂ asym. | NO ₂ sym. | ⁸ CH ₁ acceptor |
|------------------------|-----------------|-----------|-----------------|-----------------------|----------------------|---------------------------------------|
| Bands of free acceptor | | | | | | |
| a | Brownish white | 85 | 2920–2380 | 1520 | 1350 | 855,760 |
| b | Buff | 84 | 2860–2240 | 1525 | 1340 | 849,755 |
| c | Brownish yellow | 175 | 2860–2300 | 1520 | 1340 | 840,756 |
| d | Buff | 85 | 2870–2400 | 1520 | 1338 | 852,758 |
| e | Brown | 163 | – | 1520 | 1337 | 850,745 |
| f | Buff | 75 | – | 1535 | 1335 | 850,735 |
| g | Buff | 90 | 2860–2200 | 1535 | 1335 | 855,748 |
| h | Buff | 162 | 1860–2260 | 1540 | 1350 | 850,760 |
| i | Yellow | Oily | 2860–1460 | 1530 | 1340 | 850,755 |
| j | Dark brown | 52 | 3000–2500 | 1520 | 1335 | 753 |
| k | Dark Brown | 115 | 2860–2260 | 1525 | 1340 | 842,755 |

Table 4

Characteristic IR-bands of 1:2 charge–transfer complexes of pyrimidine Schiff base with 2,4- and 2,6-dinitrophenol.

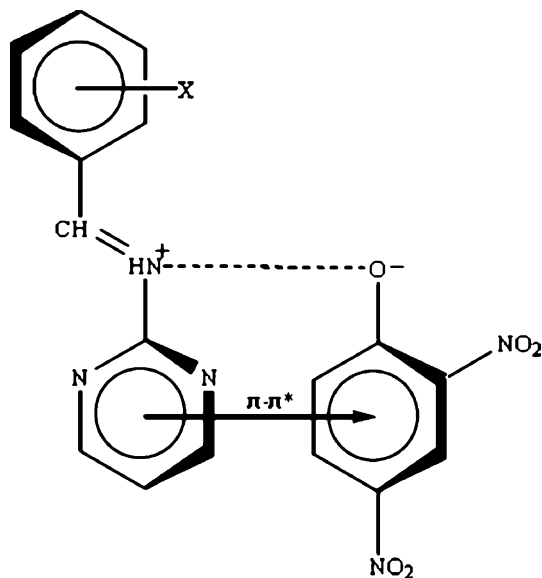
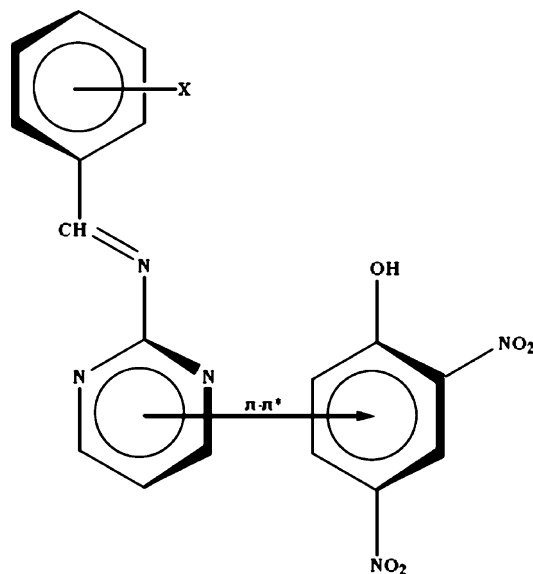
| No. | Color | m.p. (°C) | NH ⁺ | (OH | NO ₂ asym. | NO ₂ sym. | ⁸ CH ₃ acceptor |
|--------------------------------|-----------------|-----------|-----------------|-------|-----------------------|----------------------|---------------------------------------|
| Complexes of 2,4-dinitrophenol | | | | | | | |
| Bands of free acceptor | | | | 3270 | 1540,1520 | 1350 | 928,825 |
| a | Canary yellow | 112 | 2740–2300 | 3290 | 1540 | 1348,1338 | 922,818 |
| c | Yellow | 101 | 2700–2200 | 3295 | 1555,1530 | 1348,1333 | 926,810 |
| d | Yellow | 130 | 2700–2200 | 3340 | 1550,1540 | 1344 | 926,811 |
| g | Canary yellow | 136 | 2700–2200 | 3280 | 1540 | 1342 | 925,818sh |
| j | Orange yellow | 104 | 2800–2200 | – | 1555,1538 | 1345,1335 | 818 |
| Complexes of 2,6-dinitrophenol | | | | | | | |
| Bands of free acceptor | | | | 3270 | 1543,1537 | 1354 | 924,812 |
| a | Orange | 116 | 2800–2360 | 3240b | 1540,1530,1525 | 1350,1340 | 908,815 |
| c | Orange | 106 | 2820–2340 | 3220 | 1540,1530,1525 | 1350,1335 | 915,820 |
| d | Orange | 123 | 2840–2200 | 3240b | 1540,1530 | 1340s | 925sh,815 |
| g | Orange | 118 | 2800–2200 | 3250b | 1538,1530,1520 | 1335s | , 815 |
| j | Brownish orange | 87 | 2800–2400 | – | 1555,1545 | 1350,1320 | 928,820 |

The NO₂-bands of the acceptor part generally shift to lower values except in some complexes a counter shift is observed. The later observation denotes the possible existence of n–π* interaction between one NO₂ group with the hetero nitrogen facing it, if the orientation of the acceptor molecule allows.

Accordingly, the different types of interaction between the Schiff bases and the weak acidic acceptors can be represented by the formula given in Schemes 6 and 7.

The 1:2 (D:A) spectra reveal the formation of two types of molecular complexes, the same as in the 1:1 complexes. In the complexes formed through π–π* and proton transfer, the OH band of the second 2,4-dinitrophenol molecule is observed at higher wave number value in comparison to that of free acceptor. This shift may be attributed to the cleavage of the intramolecular hydrogen bond between the OH group and the o-NO₂ group. In the IR spectra of the p-N(CH₃)₂ Schiff bases, the second OH band vanishes also denoting the participation of the OH group of the second acceptor molecule in acid-base interaction with the basic N(CH₃)₂ group. The observed shift of the νC=N band to lower values is an evidence of the proton transfer interaction.

The asym NO₂ bands shift to lower values in the complexes of 2,6-dinitrophenol showing an increase of electron density on the acceptor moiety. For complexes of 2,4-dinitrophenol the νNO₂ bands shift to either higher or lower wave number. This confirms the existence of n–π* interaction.

**Scheme 6.** Structure of 1:1 CT complex of 2,4-dinitrophenol with a–d and h–k Schiff bases.**Scheme 7.** Structure of 1:1 CT complex of 2,4-dinitrophenol with e and f Schiff bases.

The bonding in the complexes may be represented as shown in Scheme 8.

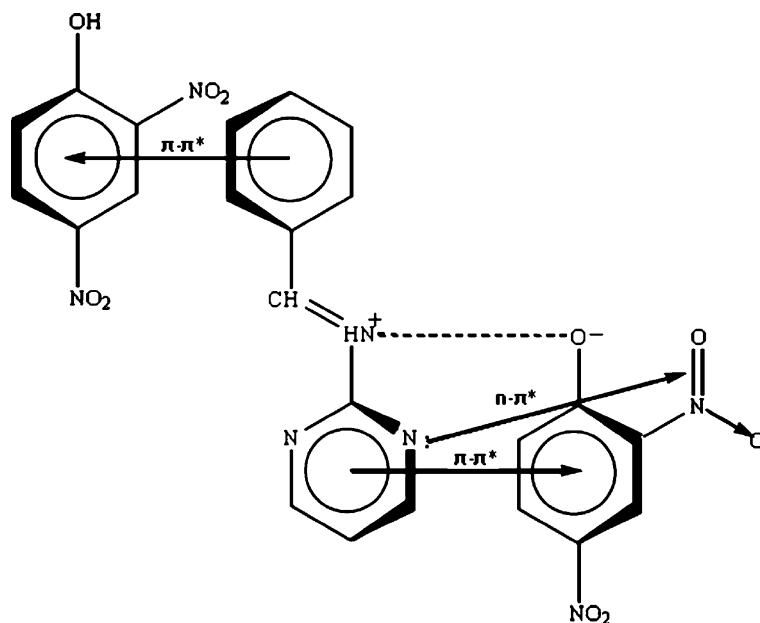
3.1.3. Complexes with non-acidic acceptors

This class comprises the CT complexes with acceptors deprived from any acidic centres (8–13). The main IR bands of some representative charge–transfer 1:1 and 1:2 complexes with picryl chloride are given in Table 5.

The only possible way of CT complex formation is electron transfer either from the π–electron system of the aromatic ring or the n–electrons of the azomethine linkage.

The NO₂ bands of the acceptors display different behavior on complex formation, depending on the type of the donor and acceptor used. In most cases the asym. NO₂ bands become broader and show some splitting in the spectra of CT complexes. This behavior indicates a higher differentiation of the energy states of the NO₂ groups in the CT complexes than in the free acceptors.

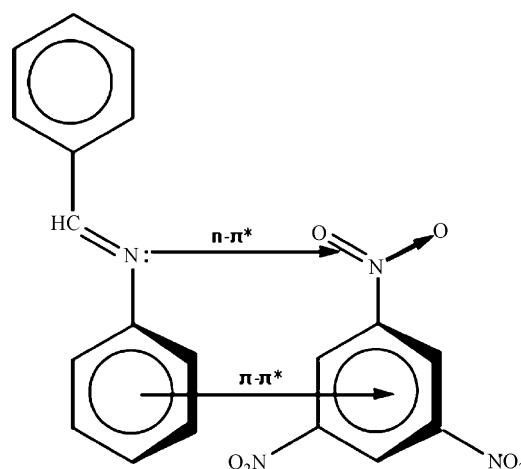
The single asym. NO₂-band of free 1,3,5-dinitrobenzene (1552 cm⁻¹) and of 1,5-difluoro-2,4-dinitrobenzene (1548 cm⁻¹) splits either to two or three bands on complex formation, one of the splitted bands appear at higher wave number and the others are displayed to lower field. In case of picryl chloride complexes the two adjacent asym. NO₂ bands (1553, 1540 cm⁻¹) split to three peaks, two bands appear at higher and the third at lower



Scheme 8. Structure of 1:2 CT complex of 2,4-dinitrophenol with a–d and h–k Schiff bases.

wave number values, while those for 1-chloro- and 1-fluoro-2,4-dinitrobenzene (1550 , 1533 cm^{-1} , 1548 cm^{-1}), become broader and shift to higher values. The shift of the NO_2 to higher values is attributed to the occurrence of secondary $n-\pi^*$ bonding forces in the complex molecule besides π -electron overlap. Such interaction is facilitated if the acceptor ring is slightly twisted so that the azomethine N-atom is positioned in front of one of the nitro groups of the acceptor ($\text{CH}=\text{N} \rightarrow \text{NO}_2$). In other cases, the orientation of the molecules make possible for one of the N-hetero ring atoms to face another NO_2 group on the acceptor molecule, thus a second $n-\pi^*$ interaction takes place. The latter case clarifies the fact that two NO_2 bands are observed at higher values. The observed shift to lower wave numbers indicates a stronger polarization which originates from increased electron density as a result of $\text{HOMO} \rightarrow \text{LUMO}$ interaction and absence of $n-\pi^*$ interaction. The formula is demonstrated in (Scheme 9).

The IR spectra of 1:2 (D:A) complexes with picryl chloride display the normal behaviors encountered in case of 1:1 CT complexes. The $\text{C}=\text{N}$ bands shift to higher wave number on complex formation, the magnitude of such shift is smaller than that observed



Scheme 9. Structure of 1:1 CT complex of trinitrobenzene with non-acidic acceptors.

Table 5
Characteristic IR bands of 1:1 and 1:2 charge–transfer complexes of pyrimidine Schiff bases with picryl chloride.

| No. | Color | m.p. ($^{\circ}\text{C}$) | $\text{NO}_{2\text{asym}}$ | $\text{NO}_{2\text{sym}}$ | $^8\text{CH}_{\text{acceptor}}$ |
|------------------------|-----------------|-----------------------------|----------------------------|---------------------------|---------------------------------|
| Bands of free acceptor | | | | | |
| 1:1 Complexes | | | 1553, 1540 | 1348 | 928, 825, 778 |
| a | Brownish yellow | 140 | 1560, 1545, 1533 | 1347 | 918, 815sh, 752 |
| b | Brownish orange | 135 | 1560, 1554, 1540 | 1353, 1345 | 922, 807, 757 |
| c | Yellow | 157 | 1565, 1549, 1540 | 1350, 1348 | 922, 805, 758 |
| d | Brownish orange | 115 | 1560, 1550, 1540 | 1350s | 922, 808, 754 |
| e | Brown | Low melting | 1560, 1550, 1540 | 1350 | 922, 810, 755 |
| f | Brown | 75 | 1560, 1550, 1540 | 1350 | 922, 812, 750 |
| g | Brown | 128 | 1560, 1554, 1540 | 1355, 1350 | 919s, –, 750 |
| h | Orange | 193ch | 1550, 1540 | 1343s | 912, 810, 742 |
| i | Brown | 138 | 1560, 1552, 1540 | 1346 | 922, 809, 760 |
| j | Brown | Low melting | 1557, 1542, 1537 | 1349 | 923, 810, 757 |
| k | Brown | 77 | 1556, 1550, 1540 | 1342, 1338 | 928, 918, 757 |
| 1:2 Complexes | | | | | |
| a | Dark brown | 153 | 1565, 1555, 1540 | 1354, 1340 | 922, 805sh, – |
| d | Dark brown | 163 | 1555, 1545 | 1350 | 922, –, 775 |
| g | Dark brown | 157 | 1536, 1550, 1540 | 1350 | 923, –, 760 |
| j | Dark brown | 63 | 1560, 1552, 1540 | 1345 | 922, –, 756 |

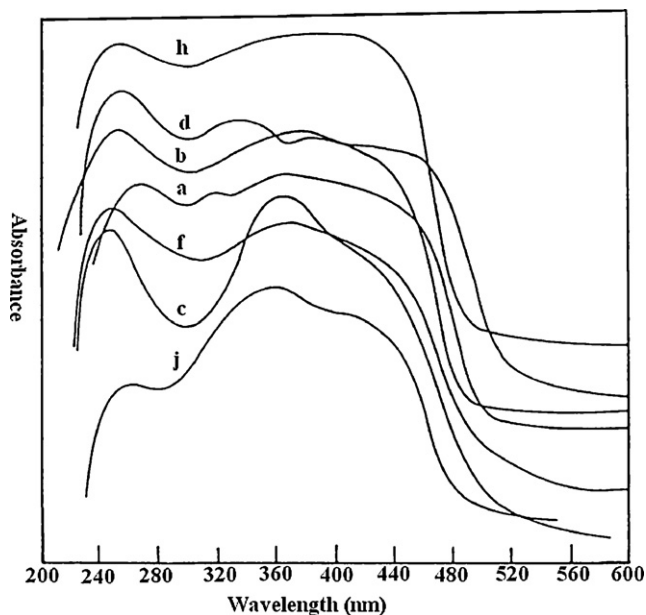


Fig. 1. Electronic absorption spectra of 1:1 charge-transfer complexes of pyrimidine Schiff bases with picric acid.

for 1:1 complexes. This may be explained on the increased localization of the π -electrons on the donor molecules as a result of the participation of both rings in complex formation as mentioned before.

3.2. Electronic absorption spectra

The electronic absorption spectra of 1:1 CT complexes of some of the investigated Schiff bases with picric acid (strong acidic acceptor), 2,5-, 2,6- and *p*-nitrophenol (weak acidic acceptors) are given in Figs. 1 and 2. The spectra display new sets of bands located on the longer wavelength side which are not observed in either the free donor or acceptor. These new bands may be broad or may appear as a shoulder. The shoulder or band may be assigned as π - π^* electronic transition. The broad shape of some bands may be attributed to the contribution of the weak n - π^* electronic interaction in the complex formation.

For the verification of this assumption, the E_{CT} values were calculated from the absorption spectra using the equation:

$$E_{CT} = \frac{1239.9}{\lambda_{CT} \text{ (nm)}} \text{ eV}$$

The results are given in Table 6 and compared with the theoretical values calculated using the relation given by Briegleb [28,29].

$$E_{CT} = I_p - E_A + C$$

where I_p is the ionization potential of the donor, E_A is the electron affinity of the acceptor and C is the coulomb force between the electron transferred and the positive hole left behind (4.7 eV) [28,29]. The observed and calculated E_{CT} values, are nearly concordant favoring their assignments as charge-transfer bands.

3.3. Nuclear magnetic resonance studies

The ^1H NMR spectra of some of the prepared Schiff bases and some selected nitrobenzene acceptors are studied to throw more insight on the molecular structure and types of interaction occurring in such complexes. Based on the IR studies, the CT complexes are classified to two main types, complexes formed through

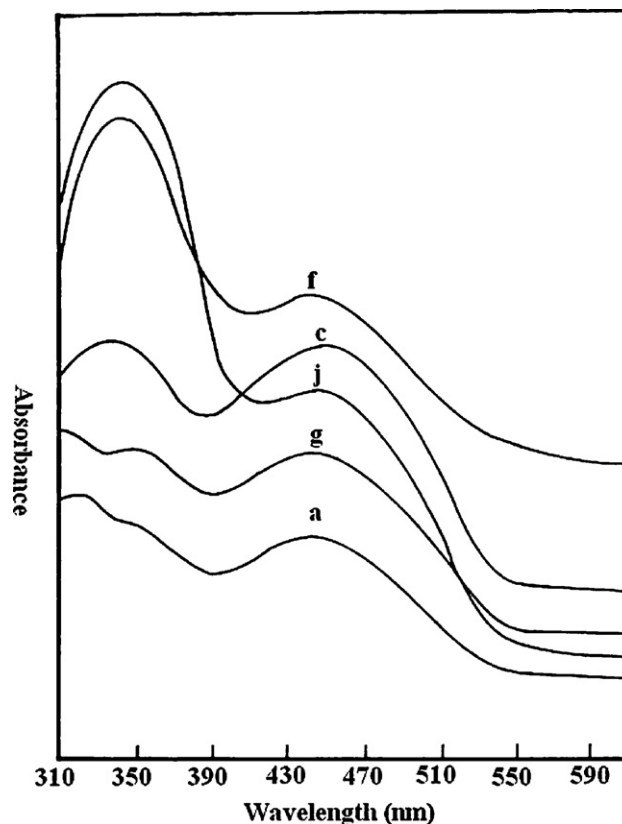


Fig. 2. Electronic absorption spectra of some charge-transfer complexes (1:1) of pyrimidine Schiff bases with 2,6-dinitrophenol.

Table 6
Electronic absorption spectral data of some 1:1 charge-transfer complexes.

| No. | X | λ_{max} (nm) | E_{CT} (eV) | |
|--------------------------------------|--|----------------------|---------------|-------|
| | | | Obs. | Calc. |
| Complexes with picric acid | | | | |
| 1 | H | 380 | 3.26 | 2.63 |
| 2 | <i>o</i> -OH | 430 | 2.88 | 2.68 |
| 3 | <i>p</i> -OH | 410 | 3.02 | 2.74 |
| 4 | <i>p</i> -OCH ₃ | 380 | 3.26 | 2.70 |
| 5 | <i>p</i> -NO ₂ | 420 | 9.95 | 2.94 |
| 6 | <i>p</i> -Cl | 400 | 3.09 | 2.63 |
| 7 | <i>p</i> -N(CH ₃) ₂ | 420 | 2.95 | 3.25 |
| Complexes with 2,5-dinitrophenol | | | | |
| a | | | 2.88 | |
| c | | 430sh | 2.82 | |
| d | | 440 | – | |
| f | | – | 2.88 | |
| g | | 430sh | – | |
| Complexes with 2,6-dinitrophenol | | | | |
| a | | 450 | 2.76 | |
| c | | 450 | 2.76 | |
| f | | 446 | 2.78 | |
| g | | 450 | 2.76 | |
| j | | 440 | 2.82 | |
| Complexes with <i>p</i> -nitrophenol | | | | |
| c | | 350sh | 3.54 | |
| d | | 390 | 3.18 | |
| g | | 350sh | 3.54 | |
| j | | 350sh | 3.54 | |

Table 7
The ¹H NMR (values for some charge-transfer complexes.

| No. | D:A | Signals of donor part | | | | | | Signals of acceptor part | | | | | | |
|--------------------------------------|-----|------------------------|----------------|----------------|----------------|-------|-------|--------------------------|----------------|----------------|----------------|----------------|-----------------|-------|
| | | Signals of benzal ring | | | | | | Signals of hetero ring | | | | | | |
| | | H ² | H ³ | H ⁵ | H ⁶ | CH | OH | H ² | H ³ | H ⁴ | H ⁵ | H ⁶ | NH ⁺ | |
| Complexes with picric acid (1) | | | | | | | | | | | | | | |
| Signals of free acceptor | | | | | | | | | | | | | | |
| J | 1:1 | 8.70 | 8.70 | 8.70 | 8.70 | 9.00 | - | - | 8.46 | 8.67 | 8.20 | 8.20 | 8.20 | 6.16 |
| J | 1:2 | 8.70 | 8.70 | 8.70 | 8.70 | 9.20 | - | - | 8.65 | 7.05 | 8.20 | 8.20 | 8.20 | - |
| Complexes with 2,4 dinitrophenol (4) | | | | | | | | | | | | | | |
| Signals of free acceptor | | | | | | | | | | | | | | |
| C | 1:1 | 7.80 | 7.20 | 7.20 | 7.80 | 9.85 | 8.30 | - | 9.20 | 8.40 | 7.30 | 8.35 | 8.50 | 10.80 |
| F | 1:1 | 8.20 | 7.50 | 7.50 | 8.20 | 9.20 | - | - | 8.30 | 6.65 | 8.70 | 8.50 | 8.50 | 7.20 |
| Complexes with 2,5 dinitrophenol (5) | | | | | | | | | | | | | | |
| Signals of free acceptor | | | | | | | | | | | | | | |
| J | 1:1 | 7.90 | 7.80 | 7.80 | 7.90 | 9.60 | - | - | 8.46 | 8.30 | 8.61 | 8.05 | 11.63 | 8.20 |
| Complexes with p-nitrophenol (7) | | | | | | | | | | | | | | |
| Signals of free acceptor | | | | | | | | | | | | | | |
| F | 1:1 | 8.45 | 7.80 | 7.80 | 8.45 | 10.40 | - | - | 8.30 | 6.60 | 7.83 | 6.90 | 9.83 | 7.20 |
| Complexes with trinitrobenzene (9) | | | | | | | | | | | | | | |
| Signals of free acceptor | | | | | | | | | | | | | | |
| C | 1:1 | 7.70 | 6.70 | 6.70 | 7.70 | 9.40 | 10.00 | - | 8.46 | 9.10 | 8.46 | 8.30 | 9.40 | 8.30 |
| J | 1:1 | 7.80 | 7.85 | 7.85 | 7.80 | 9.75 | - | - | 8.80 | 6.85 | 9.40 | 8.30 | 9.40 | 9.40 |

electron transfer only and those formed through proton transfer in addition to electron transfer.

The ¹H NMR spectra of the CT complexes formed through electron transfer only compared to those of the free components reveal a shift of the signals due to the protons of the acceptor towards higher fields, while those of the donor are shifted to lower fields. This behavior is interpreted on the basis of increased shielding of the acceptor protons and decreased on those of the donor which results from the intermolecular π - π^* CT interaction. It is clear from Table 7 that, the chemical shifts of the hetero ring protons are greater than those for the benzal ring protons. This confirms the previous assumption that the hetero ring is the moiety contributing to the CT interaction. An exception is the p-N(CH₃)₂ Schiff base where the protons of the N-dimethyl group exhibit a pronounced shift, confirming that the benzal ring is the origin of the π - π^* electronic interaction for this derivative (j). The above behavior comprises the CT complexes formed with non-acidic and some weak acidic acceptors.

The ¹H NMR spectra of complexes involving proton transfer display some changes in comparison to those of their constituents. In the spectra, the signal due to the OH-group of acceptor is no more observed, meanwhile, a new signal with an integration value equivalent to one proton is observed at about 4.1 ppm. This signal is assigned to the new centre (=N-H) formed through the transfer of the OH proton of the acceptor to the azomethine group of the donor. Such conclusion is in good agreement with that reached previously through IR studies.

It is noteworthy that, in the 1:1 complex of (j) with picric acid, the signals of the protons of the methyl group in N(CH₃)₂ become broad and shift to lower field, this is taken as a further proof that the proton of the acceptor is attached to the dimethylamine nitrogen and not to the azomethine group. For the 1:2 complex, the two rings, the benzal and the hetero, are contributing to the charge-transfer interaction and both the azomethine and the dimethylamine nitrogens are involved in proton transfer which is supported by the disappearance of the acceptor OH-proton signal and the existence of two signals at 3.8 and 4.1 ppm due to the ⁺NH(CH₃)₂ and C=⁺NH protons, respectively.

4. Conclusion

The IR spectra reveal that all strong acidic and some of the weak acidic acceptors form charge-transfer complexes with the donors through π - π^* electronic transfer from the donor (hetero-ring for a-i and benzal ring for j) to the acceptor molecule in addition to proton transfer from the acceptor to the donor.

For non acidic and some weak acidic acceptors interactions are only through π - π^* electron transfer. In some complexes secondary bonding forces, namely n- π^* interaction, are operative besides the aforementioned interactions whenever the orientation of the molecules permits.

The ultraviolet absorption spectra of some representative charge-transfer complexes reveal the presence of a new band at the longer wavelength region which was not observed in the spectra of either the free donor or free acceptor such band is assigned to the (HOMO-LUMO) π - π^* interaction (CT band). In some cases, the observed band is very broad and of composite nature. This is taken as an indication for n- π^* interaction for complexes showing it.

The nuclear magnetic resonance studies were in good agreement with those obtained from IR studies.

References

- [1] K.C. Emregul, E. Duzgun, O. Atakol, Corros. Sci. 48 (2006) 873.
- [2] R. Drozdak, B. Allaert, N. Ledoux, I. Dragutan, V. Dragutan, R. Verpoort, Coord. Chem. Rev. 249 (2005) 3055.

- [3] J.L. Sessler, P.J. Melfi, G. Dan Pantos, *Coord. Chem. Rev.* 250 (2006) 816.
- [4] C.J. Yang, S.A. Jenekhe, *Macromolecules* 28 (1995) 1180.
- [5] S. Destri, I.A. Khotina, W. Porzio, *Macromolecules* 31 (1998) 1079.
- [6] M. Ggrigoras, O. Catanescu, C.I. Simonescu, *Rev. Roum. Chim.* 46 (2001) 927.
- [7] I. Kaya, A.R. Vilayetoglu, H. Mart, *Polymer* 42 (2001) 4859.
- [8] D.R. Larkin, *J. Org. Chem.* 55 (1990) 1563.
- [9] J. Vanco, O. Svajlenova, E. Racanska, J. Muselik, J. Valentova, *J. Trace Elem. Med. Biol.* 18 (2004) 155.
- [10] B. Jarz, abek, B. Kaczmarczyk, D. Sek, *Spectrochim. Acta Part A* 74 (2009) 949–954.
- [11] R.D. Kross, V.A. Fassel, *J. Am. Chem. Soc.* 79 (1957) 38.
- [12] G. Briegleb, H. Della, *Z. Phys. Chem. (Frankfurt)* 24 (1960) 359.
- [13] R.M. Issa, M.M. Elessawey, *Z. Phys. Chem. (Leipzig)* 253 (1973) 96.
- [14] A.M. Hindawey, A.M.G. Nassar, R.M. Issa, *Acta Chem. Hung.* 88 (1976) 341; A.M. Hindawey, A.M.G. Nassar, R.M. Issa, *Acta Chem. Hung.* 92 (1977) 263.
- [15] Y.M. Issa, A.L. Elansary, M. Gaber, R.M. Issa, *Acta Chem. Hung.* 116 (1984) 273.
- [16] J. Weinstein, E. McIninch, *J. Am. Chem. Soc.* 82 (1960) 6064.
- [17] J.E. Kovacic, *Spectrochim. Acta A* 23 (1967) 183.
- [18] A.M. Hindawey, Y.M. Issa, R.M. Issa, H.F. Rizk, *Acta Chem. Hung.* 112 (1983) 415.
- [19] M. Gaber, G.B. Mohammed, M. AbdelGhafer, *J. Chem. Soc. Pak.* 9 (1987) 23.
- [20] O.L. Tombesi, M.A. Frontera, M.A. Tomas, M.A. Bafajoz, *Appl. Spectrosc.* 47 (1993) 123.
- [21] O.L. Tombesi, M.A. Tomas, M.A. Bafajoz, *Appl. Spectrosc.* 46 (1992) 873.
- [22] Y.M. Issa, N.A. Darwish, H.B. Hassib, *Egypt J. Chem.* 34 (1991) 87.
- [23] S.S. Badawy, A.F. Shoukry, Y.M. Issa, *Egypt J. Chem.* 34 (1991) 41.
- [24] M.M. Shoukry, R. Kousini, *Bull. Soc. Chem. Fr.* 128 (1991) 465.
- [25] A.L. Elansary, N.A. Darwish, Y.M. Issa, Y.M.H.B. Hassib, *Egypt J. Chem.* 33 (1990) 129.
- [26] A.M. Hindawey, Y.M. Issa, Y.A. Marghalani, R.M. Issa, *Monsatsh. Chem.* 111 (1980) 1143.
- [27] L.J. Bellamy, *The Infrared Spectra of Complexes Molecules*, Methuen, London, 1958.
- [28] G. Briegleb, *Angew. Chem.* 76 (1964) 326.
- [29] G. Briegleb, J. Czekalla, A. Hauser, *Z. Phys. Chem.* 21 (1959) 99.