Commun. Fac. Sci. Univ. Ank. Serie B
V. 32, pp. 75-86 (1986)

# PREPARATION AND SPECTROSCOPIC INVESTIGATION OF MOLECULAR COMPLEXES OF SUBSTITUTED ACETANILIDES WITH SOME TRINITROBENZENES

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(Received in June 1986, Accepted in September 1986)

SUMMARY

The solid molecular complexes formed between substituted acetanilides and trinitrobenzenes are prepared and investigated by element analysis, IR and $^1$H NMR spectroscopy. The results of element analysis confirm the formation of 1:1 complexes in a pure state. The spectral changes reveal that picric acid forms complexes with $\pi$-$\pi^*$, n-$\pi^*$ electronic interactions and proton transfer while picrylchloride and trinitrobenzene result their complexes through $\pi - \pi^*$ and n - $\pi^*$ transitions. The results are confirmed bv $^1$H NMR.

## INTRODUCTION

The existence of molecular complexes between substituted nitrobenzenes and aromatic hydrocarbons has long been recognized. Mulliken suggested that the formation of molecular complexes from two aromatic molecules can arise from the transfer of an electron from a $\pi$ - molecular orbital of the donor to a vacant $\pi^*$- molecular orbital of the acceptor molecule(Mulliken, 1950; 1952; 1952). The possibility of n-$\pi^*$ interaction was also illustrated.

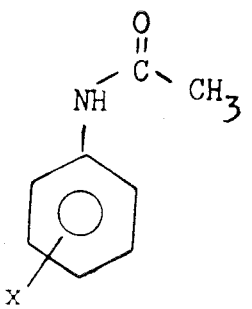
Molecular complexes of N-substituted anıline derivatives as donors and nitrobenzenes as acceptors were the subject of several investigations (El-Kholy, 1980; Hindaway, 1980; Dale, 1954; Bailey, 1963; Ross, 1957). Some of these were concerned mainly with the determination of their physical constants (K, $\triangle$H, $\triangle$S) using UV absorption spectrophotometry. (Bailey, 1963;Ross, 1957).

In the present investigation, the solid complexes formed between some acetanilide derivatives and picric acid, picrylchloride and trinitrobenzene are prepared and characterized by element analysis, IR and $^1$H NMR spectroscopy.

ISSN - 0570-1414, Ankara Üniversitesi Basımevi

## EXPRIMENTAL

The compounds used in the present investigation were pure grade chemicals from BDH. The substituted acetanilides were prepared by the previously described method (Vogel, 1962). The resulting compounds were recrystallized to constant melting point. The following substituted acetanilides were used as donors:




where x = H (a), o-Cl (b), m-Cl (c), p-Cl (d), p-Br (e), o-$CH_3$(f), m-$CH_3$(g),p-$CH_3$(h), o-$OCH_3$(i), m-$OCH_3$(j), p-$OCH_3$(k), o-$NO_2$(l), m-$NO_2$(m), p-$NO_2$(n), o-COOH(o), m-COOH(p) p-COOH (q), p-N $(CH_3)_2$(r), 2,4-di-Cl (s), p-$COCH_3$ (t)

The acceptors used in this investigation are picric acid (I), picrylchloride (II) and trinitrobenzene (III).

The solid complexes were prepared by mixing hot saturated solutions of the donor and the acceptor (0.01 mole each) in absolute ethanol. The solid complexes separate out readily with acceptor (I) while with (II) and (III) the complexes were obtained on standing. The solids obtained were purified by either boiling with or recrystalization from ethanol.

The IR spectra were recorded in KBr matrix on a Unicam SP 1000 spectrometer. The $^1H$ NMR spectra were obtained in DMSO using Varian EM-390 90 MHz NMR spectrophotometer using TMS as internal standard. The prepared molecular complexes were subjected to element analyses at the microanalytical center, Cairo University. The results are very satisfactory for 1:1 complex (donor: acceptor) Tables (1 and 2). Melting points are uncorrected.

Table I

Melting point, colour and element analysis of molecular complexes of acetanilides with picric acid

| Donor | Colour | m.p.°C | C % | | H % | | N % | | Cl % | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Calc. | found | Calc. | found | Calc. | found | Calc. | found |
| a | yellow | 66 | 46.15 | 45.90 | 3.29 | 2.91 | 15.38 | 15.51 | —— | —— |
| b | yellow | 60 | 42.15 | 42.10 | 2.76 | 3.22 | 14.05 | 13.85 | 8.90 | 9.10 |
| d | yellow | 95 | 42.15 | 42.00 | 2.76 | 3.40 | 14.05 | 14.10 | 8.90 | 8.50 |
| f | yellow green | 68 | 47.62 | 47.12 | 3.70 | 3.63 | 14.81 | 14.59 | — | — |
| g | yellow green | 60 | 47.62 | 47.30 | 3.70 | 3.45 | 14.81 | 14.93 | — | — |
| h | yellow | 85 | 47.62 | 47.24 | 3.70 | 3.92 | 14.81 | 14.69 | — | — |
| i | orange | 83 | 45.68 | 46.12 | 3.55 | 4.00 | 14.21 | 14.40 | — | — |
| k | green yellow | 74 | 45.68 | 46.20 | 3.55 | 3.90 | 14.21 | 14.35 | — | — |
| l | orange | 48 | 41.07 | 40.80 | 2.93 | 3.10 | 17.11 | 16.93 | — | — |
| m | yellow | 98 | 41.07 | 40.70 | 2.93 | 2.65 | 17.11 | 17.00 | — | — |
| n | yellow | 108 | 41.07 | 40.70 | 2.93 | 2.70 | 17.11 | 17.19 | — | — |
| o | yellow | 111 | 44.12 | 43.72 | 2.94 | 2.75 | 13.72 | 13.87 | — | — |
| p | yellow | 179 | 44.12 | 43.90 | 2.94 | 2.81 | 13.72 | 13.69 | — | — |
| q | yellow | 157 | 44.12 | 44.00 | 2.94 | 2.63 | 13.72 | 13.96 | — | — |
| r | dark green | 202 | 47.41 | 46.95 | 3.95 | 3.62 | 17.28 | 16.98 | — | — |
| s | yellow green | 99 | 38.80 | 38.37 | 2.31 | 2.50 | 12.93 | 13.21 | 16.16 | 16.37 |
| t | yellow | 97 | 47.29 | 47.09 | 3.44 | 3.60 | 13.78 | 14.00 | — | — |

Teble II

Melting point, colour and element analysis of molecular complexes of acetanilides with picrylchloride

| Donor | Colour | m.p.°C | % C | | H % | | N % | | Cl % | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Calc. | found | Calc. | found | Calc. | found | Calc. | found |
| a | yellow | 65 | 43.96 | 44.20 | 2.87 | 2.89 | 14.64 | 14.56 | 9.28 | 9.36 |
| c | yesllow | 70 | 40.29 | 39.87 | 3.39 | 3.52 | 13.46 | 13.62 | 17.03 | 17.19 |
| d | yellow | 68 | 40.29 | 40.53 | 3.39 | 3.48 | 13.46 | 13.94 | 17.03 | 17.12 |
| e | yellow | 92 | 36.40 | 36.17 | 2.16 | 2.51 | 12.13 | 12.43 | — | — |
| f | yellow | 56 | 45.39 | 45.46 | 3.27 | 3.38 | 14.12 | 14.21 | 8.95 | 8.46 |
| g | yellow | 71 | 45.39 | 45.14 | 3.27 | 3.19 | 14.12 | 14.51 | 8.95 | 8.39 |
| h | yellow | 77 | 45.39 | 45.51 | 3.27 | 4.34 | 14.12 | 14.37 | 8.95 | 8.79 |
| i | orange | 79 | 43.64 | 43.88 | 3.15 | 2.81 | 14.49 | 14.18 | 8.60 | 8.31 |
| j | brown | 74 | 43.64 | 43.92 | 3.15 | 2.93 | 14.49 | 14.13 | 8.60 | 8.43 |
| k | brown | 60 | 43.64 | 43.73 | 3.15 | 2.74 | 14.49 | 14.67 | 8.60 | 8.19 |
| l | yellow | 52 | 39.29 | 38.98 | 2.57 | 2.57 | 16.37 | 16.21 | 8.30 | 8.62 |
| m | pale yellow | 98 | 39.29 | 39.36 | 2.57 | 2.72 | 16.37 | 16.72 | 8.30 | 8.80 |
| n | yellow | 77 | 39.29 | 39.43 | 2.57 | 2.94 | 16.37 | 16.66 | 8.30 | 8.71 |
| o | yellow | 135 | 42.20 | 42.44 | 2.58 | 3.00 | 13.14 | 13.42 | 8.32 | 7.92 |
| p | pale yellow | 83 | 42.20 | 42.38 | 2.58 | 2.83 | 13.14 | 13.36 | 8.32 | 7.96 |
| q | pale yellow | 170 | 42.20 | 42.17 | 2.58 | 2.84 | 13.14 | 13.29 | 8.32 | 7.89 |
| r | black | 80 | 45.12 | 44.51 | 3.52 | 3.15 | 16.45 | 16.17 | 8.34 | 8.53 |
| s | green yellow | 72 | 37.22 | 37.48 | 1.99 | 2.31 | 12.40 | 12.19 | 23.58 | 23.93 |
| t | yellow | 74 | 45.12 | 45.30 | 2.35 | 2.80 | 13.16 | 13.26 | 8.34 | 8.63 |

## RESULTS AND DISCUSSION

The results of element analyses of the molecular complexes under investigation, Tables 1 and 2 are in good agreement with those required for 1:1 complexes. Compounds isolated from mixtures containing twice as many acceptors than donors (in a trial to test the possibility for the existence of 1:2 complexes) were only 1:1 complexes. This is in accordance with previous conclusions that the presence of a donating $\pi$ – system is essential for CT complex formation (Issa, 1981).

The acceptors used in the present investigation are either acidic molecules (I) or neutral molecules (II) and (III). Since the donor molecules under investigation have obvious basic character, then it is acceptable that their behaviour towards acceptor (I) would be different from that towards (II) and (III). In the former case, the charge transfer interaction is expected to take place through electron transfer from the donor molecule to the acceptor and proton transfer from the acceptor molecule to the basic center in the donor, while electron transfer only is expected with acceptors (II) and (III). Accordingly each type of molecular complexes is considered separately.

## MOLECULAR COMPLEXES WİTH PİCRİC ACİD (I)

The IR spectra of the molecular complexes formed when picric acid is allowed to react with the donors under investigation exhibit some dramatic changes which are used to elucidate both the type of bonding and the structure of these complexes. These changes may be summarized in the following:

The $\nu_{NH}$ bands of the donor appearing within the wave number range 3300-3200 $cm^{-1}$ are not observed in the IR spectra of the molecular complexes (El-Ansary, 1985). Meanwhile a group of weak to medium bands are observed within the 3000-2400 $cm^{-1}$ range. These bands are attributed to the stretching vibration of a hydrogen atom attached to a positively charged nitrogen atom ($N^{+}$-H). This assignment is in agreement with those previously reported for aniline salts (Bellanato, 1960). This group is formed through the transfer of a proton from the acidic OH-group of picric acid (pKa = 0.38) to the basic nitrogen atom of the donor molecule (Weast, 1978; 1979). This is also confirmed by the disappearance of the $\nu_{OH}$ band of PiOH.

Table III
Colour and melting point of molecular complexes of acetanilides with trinitrobenzene

| Donor | Colour | m.p.°C | Donor | Colour | m.p.°C |
|---|---|---|---|---|---|
| a | buff | 75 | k | brown | 82 |
| b | brown | 58 | l | yellow | 115 |
| c | buff | 93 | m | buff | 116 |
| d | buff | 110 | n | buff | 168 |
| e | buff | 120 | o | buff | 136 |
| f | pale brown | 81 | p | buff | 218 |
| g | buff | 83 | q | buff | 221 |
| h | buff | 85 | r | dark brown | 151 |
| i | yellow orange | 119 | s | brown | 102 |
| j | buff | 76 | t | pale brown | 129 |

For donors l, m and n, IR spectra of the complexes display the $\nu_{OH}$ band of picric acid at 3370, 3310 and 3290 $cm^{-1}$ respectively. Also the $\nu_{NH}$ of the donors are observed at 3120 $cm^{-1}$. This may be taken as evident that proton transfer does not participate in the formation of these complexes.

The amide I band ($\nu_{C=O}$) mostly exhibit a shift to lower wave number on complex formation. This is attributed to decreased polarization of the C=O under the influence of the electron withdrawing $NH_2^+$ group especially in presence of electron donor group in the acetanilides. For donors o,p and q containing a COOH group, a slight shift to higher wave number is observed.

Picric acid exhibits three $\nu_{asym}$ $NO_2$ bands which shift to lower wave number on complex formation with donors a, l, m, n, s and t. This shift indicates the increased polarization of the $NO_2$ groups in the molecular complexes. This behaviour results from the $\pi - \pi^*$ charge transfer interaction. For other donors, the higher $\nu_{asym}$ $NO_2$ band shifts to higher wave number. This can be explained by invoking the occurance of an n-$\pi^*$ interaction between an n-electron on the substituent with a vacant $\pi$–level on the nitro group facing it. This interaction has a high possibility for o- and p- substituents having n-electrons. The $\nu_{sym}$ $NO_2$ band shifts to lower wave numbers, which is in accordance with previous studies (Issa, 1981).

The $\gamma_{CH}$ band of the acceptor (PiOH) is shifted to lower wave numbers (Table 4) while those of acetanilides (Table 5) are mostly shifted to higher wave numbers. These shifts are ascribed to increased polarization of the CH bonds in the acceptor part and the reverse in the donor part of the complex.

In general, the above results lead to the conclusion that picric acid form molecular complexes with acetanilides through proton

Table IV

Main IR bands of the acceptor part in molecular complexes of acetanilides with trinitrobenzenes ($cm^{-1}$)

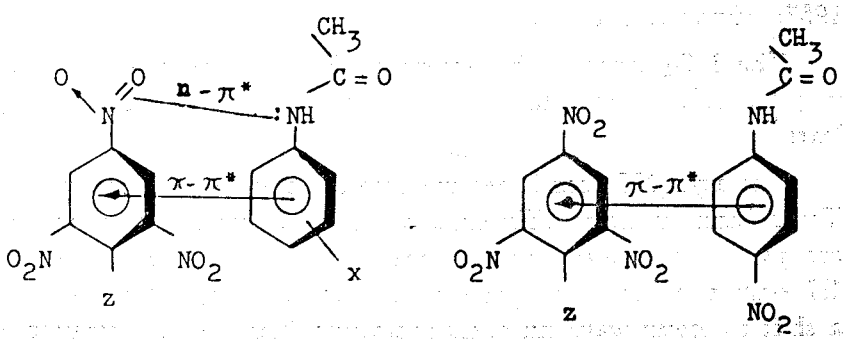
| Donor | x | picric acid | | | picrylchloride | | | trinitrobenzene | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $NO_2$ asym | $NO_2$ sym | $\gamma_{CH}$ | $NO_2$ asym | $NO_2$ sym | $\gamma_{CH}$ | $NO_2$ asym | $NO_2$ sym | $\gamma_{CH}$ |
| Free acceptor | | 1555,1540,1530 | 1350 | 784 | 1553,1540 | 1348 | 788 | 1552 | 1347 | 920 |
| a | H | 1540,1527,1520 | 1340 | 782 | 1565,1545,1520 | 1350 | 775 | 1550,1540 | 1355 | 910 |
| b | o-Cl | 1560,1530,1520 | 1340 | 776 | ——— | —— | —— | 1545,1532 | 1350 | 915 |
| c | m-Cl | ——— | —— | —— | 1555,1545,1535 | 1345 | 775 | 1550,1540 | 1355 | 910 |
| d | p-Cl | 1555,1545,1520 | 1340 | 790 | 1555,1545,1530 | 1350 | 775 | 1540,1535 | 1350 | 910 |
| e | p-Br | ——— | —— | —— | 1558,1535,1525 | 1345 | 755 | 1555,1540 | 1358 | 912 |
| f | o-$CH_3$ | 1555,1545,1523 | 1340 | 773 | 1555,1540,1527 | 1350 | 755 | 1550,1540 | 1370 | 920 |
| g | m-$CH_3$ | 1558,1540,1523 | 1343 | 790 | 1550,1535 | 1350 | 755 | 1542,1538 | 1350 | 905 |
| h | p-$CH_3$ | 1558,1545,1523 | 1340 | 785 | 1555,1540,1530 | 1350 | 755 | 1550,1530 | 1350 | 905 |
| i | o-$OCH_3$ | 1560,1535,1521 | 1342 | 778 | 1555,1545,1535 | 1350 | 755 | 1552,1532 | 1350 | 910 |
| j | m-$OCH_3$ | ——— | —— | —— | 1550,1535,1525 | 1345 | 770 | 1555,1540 | 1350 | 900 |
| k | p-$OCH_3$ | 1558,1540,1522 | 1342 | 775 | 1560,1550,1530 | 1345 | 770 | 1540,1530 | 1350 | 910 |
| l | o-$NO_2$ | 1550,1525 | 1350 | 790 | 1555,1545,1525 | 1350 | —— | 1540 | 1335 | 915 |
| m | m-$NO_2$ | 1535,1525 | 1350 | 790 | 1555,1535,1528 | 1350 | 755 | 1555 | 1350 | 895 |
| n | p-$NO_2$ | 1555,1535,1530 | 1355 | 785 | 1565,1550,1535 | 1350 | 750 | 1550 | 1350 | 912 |
| o | o-COOH | 1558,1549,1535 | 1350 | 780 | 1545,1535,1525 | 1350 | 770 | 1540 | 1350 | 900 |
| p | m-COOH | 1565,1550 | 1350 | 780 | 1563,1550,1535 | 1350 | 755 | 1550 | 1352 | 895 |
| q | p-COOH | 1560,1550,1530 | 1350 | 780 | 1555,1540,1527 | 1350 | 755 | 1552 | 1350 | 920 |
| r | p-$N(CH_3)_2$ | 1560,1542,1525 | 1330 | 780 | 1555,1550,1535 | 1350 | 755 | 1560,1540 | 1350 | 910 |
| s | 2,4-di-Cl | 1550,1545,1532 | 1350 | 790 | 1555,1545,1535 | 1350 | 765 | 1555,1542 | 1380 | 900 |
| t | p-$COCH_3$ | 1550,1532 | 1350 | 788 | 1558,1550,1535 | 1350 | 760 | 1550,1540 | 1350 | 910 |

Table V: Main IR-bands of the donor part in molecular complexes of acetanilides with trinitrobenzenes ($cm^{-1}$)

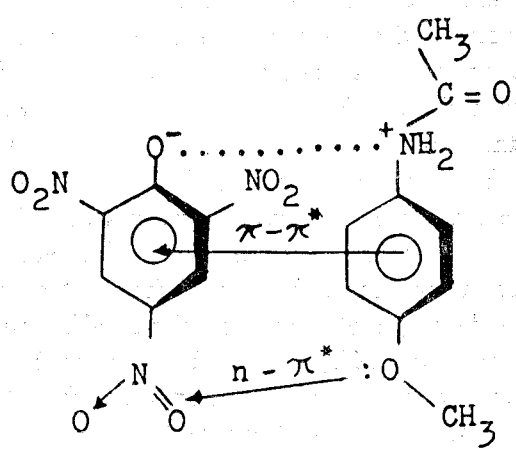
| Donor | free donor | | | picric acid | | | picrylchloride | | | trinitrobenzene | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\nu_{NH}$ | C=O | $\gamma_{CH}$ | $-N^+H_2$ | C=O | $\gamma_{CH}$ | $\gamma_{NH}$ | C=O | $\gamma_{CH}$ | νNH | C=O | $\gamma_{CH}$ |
| a | 3280,3240 | 1658 | 760,690 | 3250–2300 | 1630 | 765,695 | 3290,3240 | 1670 | 765,700 | 3040 | 1690 | 760,720 |
| b | 3270,3250 | 1660 | 758,717 | 3050–2320 | 1636 | 760,730 | — | — | — | 3300,3090 | 1670 | 760,730 |
| c | 3290,3280 | 1672 | 903,872,790 | — | — | — | 3325 | 1670 | 915,882,822 | 3300,3100 | 1660 | 920,885,800 |
| d | 3300,3270 | 1672,1665 | 845,832,755 | 3100–2320 | 1650 | 845,824,742 | 3310,3270 | 1665 | 840,830,752 | 3300,3120 | 660 | 850,840,765 |
| e | 3280,3230 | 1670 | 835,825,748 | — | — | — | 3310,3070 | 1675 | 840,830,754 | 3300,3080 | 1660 | 845,840,750 |
| f | 3270,3230 | 1665 | 752,712 | 3090–2430 | 1630 | 760,712 | 3300 | 1650 | 755,718 | 3220,3120 | 1665 | 765,720 |
| g | 3290,3250 | 1660 | 900,880,788 | 3060–2230 | 1650 | 880,790 | 33z0 | 1660 | 920,900,790 | 3300,3120 | 1670 | 925,885,795 |
| h | 3300,3250 | 1662 | 828,822,760 | 3100–2360 | 1650 | 850,825,780 | 3320 | 1687 | 850,815,755 | 3320,3120 | 1670 | 840,825,765 |
| i | 3260,3240 | 1652 | 752,715 | 3100–2280 | 1650 | 750,717 | 3420 | 1687 | 758,717 | 3320,3120 | 1660 | 760,730 |
| j | 3295,3250 | 1657 | 900,863.770 | — | — | — | 3330 | 1660 | 915,867,790 | 3300,3120 | 1670 | 920,880,780 |
| k | 3260,3230 | 1650,1638 | 840,822,775 | 3100–2360 | 1645 | 842,830,785 | 3200,3080 | 1650 | 855,835,780 | 3300,3120 | 1660 | 860,840,795 |
| l | 3260 | 1705,1697 | 792,752,708 | ** | 1708,1638 | 00,753,710 | 3260 | 1667 | 820,793,705 | 3380,3120 | 1710 | 795,770,730 |
| m | 3300,3270 | 1685,1672 | 880,815,808 | ** | 1680,1640 | 892,825,810 | 3375 | 1680 | 887,820,805 | 3320,2120 | 1680 | 895,828,810 |
| n | 3300,3270 | 1690,1677 | 867,852,765 | ** | 1687,1640 | 870,852,785 | 3315,3285 | 1680 | 890,865,765 | 3290,3120 | 1685 | 865,855,750 |
| o | 3200 | 1688 | 792,770,703 | 3120–2400 | 1700,1638 | 795,785,700 | 3115 | 1702 | 810,780,720 | 3120 | 1690 | 800,790,715 |
| p | 3230 | 1703 | 883,780,755 | 3100–2340 | 1710,1658 | 895,810,780 | 3345 | 1714,1708 | 895,780,755 | 3350,3120 | 1715 | 895,796,765 |
| q | 3300 | 1686,1675 | 855,837,780 | 3100–2320 | 1695,1675 | 855,840,785 | 3320 | 1686,1675 | 880,850,795 | 3340,3120 | 1700 | 860,840,790 |
| r | 3270,3230 | 1655,1645 | 852,815,770 | 3080–2300 | 1692,1635 | 855,825,790 | 3360,3300 | 1685,1660 | 855,825,790 | 3300,3140 | 1670 | 860,830,770 |
| s | 3290,3260 | 1670 | 868,822,773 | 3120–2300 | 1670,1640 | 870,830,790 | 3320,3280 | 1680 | 865,850,765 | 3310 | 1675 | 870,825,770 |
| t | 3310,3260 | 1690,1673 | 858,842,765 | 3120–2420 | 1680,1640 | 855,842,785 | 3295 | 1665 | 890,820,789 | 3300,3120 | 1680 | 865,850,770 |

** not observed

transfer from the phenolic OH group of PiOH (except with nitro substituted derivatives l, m and n) to the basic center (NH group) on the acetanilides. Charge transfer interaction results from the location of an electron from the highest occupied molecular orbital (HOMO) of the donor to the lowest unoccupied molecular orbital (LUMO) on the acceptor. In addition n–π* interaction occures between substituents containing n-electrons and the nitro group facing it. Thus the CT interaction in molecular complexes belonging to this group may be represented as follows:




z = Cl (II), H (III)




Ik

Molecular complexes with picrylchloride (II) and trinitrobenzene (III)

The IR spectra of molecular complexes formed between acetanilides and picrylchloride (II) of trinitrobenzene (III) are superposition of the IR spectra of their constituents. The spectra of the complexes compared with those of their components (Tables 4 and 5) reveal an apparent shift of the $\gamma_{CH}$ bands of the acceptor to lower wave numbers while those of the donors are shifted to higher ones. This behaviour results from the increased electron density on the benzene ring of the the acceptor and its decrease on that of the donor which results from intermolecular $\pi - \pi^*$ electron transfer from the HOMO of the donor molecule to the LUMO of the acceptor molecule (Issa, 1981; Kross, 1957; Hindawey, 1983).

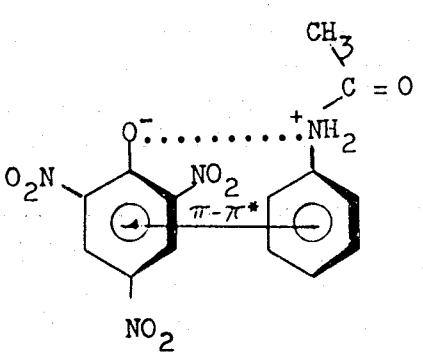
The $NO_2$ bands of the acceptors display some changes which may be useful for elucidation of the bonding in the molecular complexes.

The asym $NO_2$ bands become broadened and split in many cases. This splitting indicate differentiation of the energy states of the $NO_2$ groups. For complexes with II three peaks are observed while with III only two peaks are present. The lower energy band displays a shift to lower wave numbers indicating increased polarization of the $NO_2$ group corresponding to this band. The higher energy band almost shift to higher wave numbers (specially for II complexes) which can be accounted for by assuming the occurance of an $n-\pi^*$ interaction involving the transfer of a lone electron pair from the the nitrogen atom of the acetanilide to a $NO_2$ group facing it in the charge transfer molecule (Kross, 1957). The $n-\pi^*$ would overcome the effect of the $\pi-\pi^*$ CT interaction, hence the band is shifted to higher values. For complexes of III, the asym $NO_2$ band splits to two peaks, the first at lower wave number while the second shifts either to lower or higher values. Sometimes it retains its position, this may be due to the compansation of the $\pi-\pi^*$ effect by the $n-\pi^*$ interaction (Hindawey, 1983). For complexes of III with l, m, n, o, p and q only one asym. $NO_2$ band is observed for the acceptor. This may be attributed to the electron withdrawing effect of the substituents, thus diminishing the $n-\pi^*$ interaction.

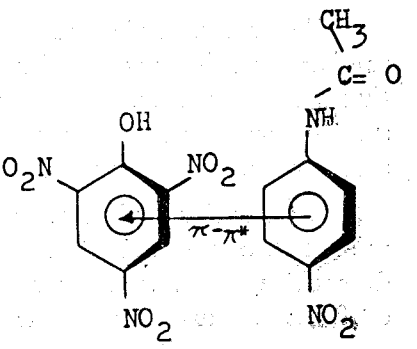
The sym. $NO_2$ bands of both acceptors II and III display shifts to higher wave numbers. This behaviour confirms the existence of CT interaction.

The higher energy NH band of the donors shifts to higher wave numbers while the low energy band exhibit counter shifts or disappears. This indicates the decreased electron density on the nitrogen atom as a result of $\pi$–$\pi^*$ and n-$\pi^*$ electron interactions.

Based on the above discussion the molecular complexes with picrylchloride or trinitrobenzene may be represented by the following:




Ia



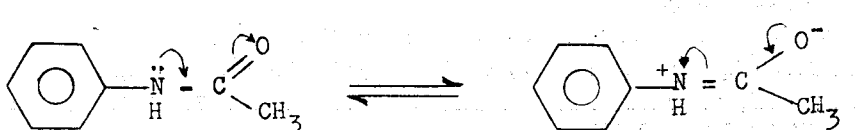

In

$^1$H NMR

A further support for the conclusions gained from the IR spectra is obtained from considering the $^1$H NMR spectra of molecular complexes in comparison to those of their constituents.

The signals due to aromatic protons of the donor part are shifted to higher $\delta$ values while those of the acceptor part exhibit reverse displacement. Such shifts are due to the decreased electron density on the donor ring and its increase on the acceptor one, which results from the intermolecular CT interaction.

The free donors exhibit the NH signal at 10.28-9.8 ppm which are shifted to higher field at 9.45-8.85 ppm on complex formation (Bennett, 1969). This shift can be explained by considering the resonance of the donor as follows:



Such resonance is prohibited or may be reversed as a results of the charge transfer interaction from the donor ring ($\pi$–$\pi^*$) and from the nitrogen atom (n–$\pi^*$).

The $^1H$ NMR spectrum of Ia exhibits broad signals at 8.9-9.2 ppm with an integration equivalent to two protons while that of the OH group of picric acid no longer exist. These signals are likely to be assigned to the $-^+NH_2$ group formed through the proton transfer from the acceptor to the donor molecule.

The spectrum of In displays two signals at 9.1 ppm and 9.35 ppm the NH and OH protons. This indicates that In complex is formed through electron transfer only confirming that strong withdrawing substituents on the donor hindered the proton transfer from picric acid molecule to the donor.

For complexes of acceptors II and III the NMR spectra display the signals of both donor and acceptor with those of the former shifted downfields and of the later exhibit a reverse displacement. Such shifts confirms the existence of the CT interaction as mentioned above.

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