

SPECTROSCOPIC INVESTIGATION OF NAPHTHALENE AND PHENANTHRENE PICRATES

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(Received October 30, 1986; revised March 18, 1987)

Charge transfer complexes of some mono- and disubstituted naphthalenes and phenanthrenes were prepared. Elucidation of the type of complexation using IR, $^1\text{Hnmr}$ and $^{13}\text{Cnmr}$ spectra was done.

Key words: NMR C.T. Complexes

INTRODUCTION

Extensive studies on charge transfer complexation using ir, uv and $^1\text{Hnmr}$ spectroscopy have been carried out [1-8]. Our present investigation will be focused on the use of ir, $^1\text{Hnmr}$ and $^{13}\text{Cnmr}$ spectra in determining the type of interaction within the usual addition complexes of some naphthalene and phenanthrene, picrates.

The intermolecular charge transfer (C.T.) was assumed to occur under the influence of a strongly acceptor molecule as picric acid where the attractive influence of three nitro groups will render it a good acceptor for the electrons donated by the donor naphthalene or phenanthrene moieties.

EXPERIMENTAL

All compounds used in the present investigation were B.D.H. pure laboratory grade. The C.T. complexes were prepared by conventional methods [1-9]. The separated solid were filtered off, washed with ethanol, then dried. The IR spectra were obtained in the usual way of C.T. complexes [1] as KBr discs using a Perkin-Elmer SP. 2000 infrared spectrophotometer. The $^1\text{Hnmr}$ spectra were recorded on a Varian EM 360 L spectrometer with tetramethylsilane as internal standard, using DMSO-d_6 as a solvent. $^{13}\text{Cnmr}$ spectra were recorded on Jeol JNM-FX 100 nmr spectrometer using the same solvent.

RESULTS AND DISCUSSION

Two types of addition complexes were expected with the compounds under investigation, namely (1) Naphthalene derivatives which yield P.T. compounds of the salt type, namely, α - and β -naphthylamines; and (2) Naphthalene and phenanthrene derivatives giving addition compounds of the molecular complex type.

These two represent the set of the compounds investigated.

I. IR spectra

(A) *Compounds of the salt type.* The addition compounds of α - and β -naphthylamines with picric acid represent an example of proton transfer (P.T.) compound. The formation of these compound takes place through a proton transfer from the OH group of picric acid to the amino group of the naphthalene derivative in addition to the intermolecular charge transfer between the aromatic rings. The main spectral changes in the spectra of such types are the following:

(i) The disappearance of νOH_2 and νOH bands, and the appearance of new bands characteristic for the $-\text{NH}_3^+$ grouping within the 2500-2800 cm^{-1} region.

(ii) νNO_2 bands at 1560 cm^{-1} and 1543 cm^{-1} (asym.) which appear double in the spectrum of the free acceptor, appear as a single broad band in the spectra of the P.T. compounds due to the destruction of the intermolecular hydrogen bonding between the OH and the O- NO_2 groups. Also the NO_2 bands are generally shifted to lower frequencies as a result of the increased electron density on the aromatic ring of the picrate ion.

(iii) The γ CH bands of the acceptor part of the P.T. compound at 785 cm^{-1} are shifted to lower wave numbers, while the γ CH bands of the naphthalene moiety are shifted to higher values. This behaviour denotes increased electron density on the picrate part and its lowering on the naphthalene ring.

Accordingly, in compounds of the salt type the bonding between the two molecules of the addition complex would occur through electrostatic attraction between the positive and negative parts, in addition to the π - π^* charge transfer.

(B) *Compounds of typical C.T. type.* The complexes formed between picric acid and phenanthrene 9-bromophenanthrene and naphthalene derivatives represent the ideal examples of C.T. type in which picric acid is a strong electron acceptor and the naphthalene or phenanthrene

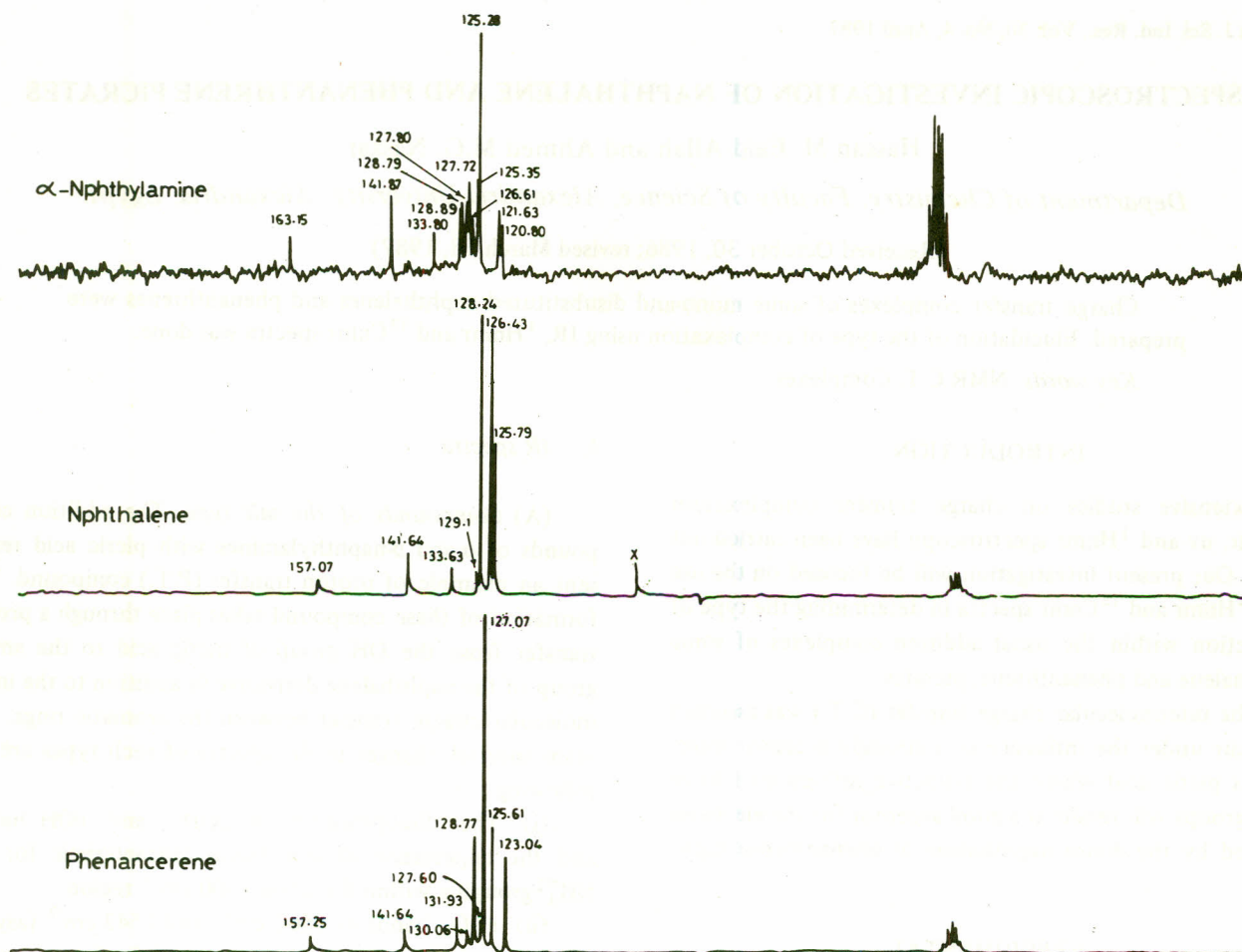


Fig. 1.

derivative is the donor. The complexes of this type are characterised by intense colours (Table 1).

The infrared spectra of these compounds are more or less a superposition of the spectra of the simple components but showing obvious shifts in band positions. The observed spectral shifts are discussed in the following:

(i) In the high frequency region, the bands corresponding to the νOH of picric acid is shifted to lower values in the spectra of the C.T. complexes due to increased π -electron density on the acceptor ring leading to a stronger hydrogen bonding within the acceptor part of the C.T. complex.

(ii) The νNO_2 bands of the acceptor in the C.T. complexes acquire a blue shift which is clearly observed within the νNO_2 asymmetric bands due to increased charge migration of the aromatic ring as a result of the C.T.

(iii) The γ CH bands of the acceptor are shifted to lower wavenumbers while those of the donors display a counter shift. This behaviour is characteristic of C.T. interaction of the π - π^* type.

II. $^1\text{Hnmr}$ Spectra

$^1\text{Hnmr}$ spectra of the free donors display two or three sets of signals within δ 7.05 – 8.61 ppm for the protons of naphthalene or phenanthrene rings, while the free acceptor (picric acid) shows a single signal at δ 8.92 ppm.

A comparison of the values of both free components and those of the C.T. complexes (Table 2) reveals the following:

(i) In the $^1\text{Hnmr}$ spectra of the complexes of the salt type the signal due to the NH_2 proton disappeared and a new signal (of three proton intensity) was observed in the region δ 6.33-6.40 corresponding to the proton of the $-\text{NH}_3^+$ group formed through a proton transfer from the OH-group of picric acid to the NH_2 group of the naphthalene derivative. The signal of the acceptor displays a shift to higher fields as the result of the increased electron density on the molecule and hence furnishing a higher shielding effect on picric acid protons in the C.T. complexes. On the other hand the signals of the donors are shifted down fields due to decreased electron density on the naphthalene ring

Table 1. Some important bands in the IR-spectra of naphthalene and phenanthrene derivatives with picric acid.

Compound No.	Donor	Compound formed	Colour	Yield %	M.P. °C	Lit M.P. °C	ν OH	ν NO ₂	γ CH	ν NH		
							asym.	sym.	Acceptor	Donor		
Values of picric acid							3110	1560, 1543	1350	785		
1. Naphthalene		M.C.	Y	98	146	148	3100	1570, 1558	1348	782	805	
2. 1-Bromonaphthalene		M.C.	Y	92	138	134	3090	1568	1552	1349	775	808
3. 1-Chloronaphthalene		M.C.	Y	95	138	137	3085	1565	1550	1350	780	808
4. 1-Methylnaphthalene		M.C.	Y	90	141	142	3100	1568	1555	1355	780	805
5. 1-Butylnaphthalene		M.C.	Y	88	103	105	3095	1566	1552	1358	780	805
6. 3,6-Dimethylnaphthalene		M.C.	Y	85	125	a	3102	1568	1554	1350	768	808
7. 1-Acetonaphthalene		M.C.	Y	80	116	116	3105	1570	1555	1360	772	806
8. Naphthalene-1-carboxaldehyde		M.C.	Y	82	95	b	3100	1565	1554	1355	770	800
9. 1-Hydroxynaphthalene		M.C.	O	78	195	c	3105	1568	1555	1348	780	795
10. 2-Hydroxynaphthalene		M.C.	O	75	158	d	3095	1565	1550	1350	776	798
11. 1,5-Dihydroxynaphthalene		M.C.	R.O.	72	112	e	3088	1568	1552	1349	772	795
12. 2-Hydroxy-1-naphthaldehyde		M.C.	O	74	121	120	3090	1572	1552	1360	768	800
13. 2-Hydroxy-1-nitrosonaphthalene		M.C.	D.R.B	70	105	f	3095	1570	1554	1352	768	804
14. Acenaphthene		M.C.	O	95	160	162	3102	1569	1550	1362	779	798
15. 1-Naphthylamine		P.T.	D.R.B	75	166	163	-	1540	1336	775	805	2800-2445
16. 2-Naphthylamine		P.T.	D.R.B	72	195	195	-	1542	1338	772	800	2775-2500
17. Phenanthrene		M.C.	O	94	142	144	3095	1565	1550	1352	778	790
18. 9-Bromophenanthrene		M.C.	Y	92	132	g	3085	1566	1555	1390	775	800

M.C. = Molecular complex, P.T. = Proton transfer complex

Y = Yellow, O = Orange, D.R.B. = Dark redish brown R.O. = redish Orange.;

a Anal. Calcd. for C₁₈H₁₅N₃O₇: C,56.1; H, 3.9; N,10.9 Found: c,56.0; H,4.1; N,11.0%. b Anal. Calcd. for; C₁₇H₁₁N₃O₈: c,56.1; H,3.9; N,10.9. Found: c,56.2; H,3.8; N,10.8%. c Anal. Calcd. for C₁₆H₁₁N₃O₈: c,51.5; H,2.9; H,11.3.; Found: C,51.6; H,2.9; N,11.2%. d Anal. Calcd. for C₁₆H₁₁N₃O₈: C, 51.5; H, 2.9; 11.3. Found: C,51.4; H,3.1; N,11.1%. e Anal. Calcd. for C₁₆H₁₁N₃O₉: C, 49.4; H,2.8; N,10.8. Found: C,49.3; H,2.7; N, 10.9%. f Anal. Calcd. for C₁₆H₁₀N₄O₉;; C,47.8; H,2.5; N,13.9 Found: c,47.9; H,2.4; N,14.0%. g Anal. Calcd. for C₂₀H₁₂Br N₃O₇:C,49.4; H,2.5;N,8.6. Found: C,49.3;; H,2.4; N,8.6%.

Table 2. ¹H Nmr chemical shifts of naphthalene and phenanthrene derivatives and their picrates^a

Donor	Picric acid moiety		Naphthalene and phenanthrene derivative δ (free)	Naphthalene and phenanthrene moiety δ	$\Delta\delta$
	δ	$\Delta\delta$			
<i>Naphthalene C.T. Complexes</i>					
Naphthalene	8.41	- 0.51	7.41,7.12	7.51,7.23	0.10,0.11
1-Bromonaphthalene	8.80	- 0.12	7.90,7.50	8.02,7.60	0.12,0.10
1-Chloronaphthalene	8.69	- 0.23	7.98,7.64	8.11,7.55	0.13,0.09
1-Methylnaphthalene	8.51	- 0.41	7.50,7.29,2.40 (s,CH ₃)	7.60,7.35,2.51(s,CH ₃)	0.10,0.60,0.11
1-Butylnaphthalene	8.68	- 0.24	7.43,7.10,2.98(t,CH ₂), 1.41(m,2CH ₂),0.90(s,CH ₃)	7.56,7.22,3.01(t, 2CH ₂) 1.50(m,2CH ₂), 0.96 (t,2CH ₃)	0.13,0.12,0.09, 0.06
3,6-Dimethylnaphthalene	8.79	- 0.13	7.71(d,2H),7.50(s,2H), 7.28(d,2H),2.51(s,CH ₃)	7.80(d,2H),7.62(s,2H) 7.30(d,2H),2.61(s,CH ₃)	0.09,0.12,0.02, 0.10
1-Acetonaphthalene	8.48	- 0.44	7.72,7.46,2.71(s,CH ₃)	7.89,7.56,2.60(s,CH ₃)	0.17,0.10,0.11
Naphthalene-1-carboxaldehyde	8.25	- 0.67	8.61,7.52,7.22,9.79 (s,CHO)	8.70,7.62,7.29,9.98 (s,CHO)	0.09,0.10,0.07,0.19
1-Hydroxynaphthalene	8.50	- 0.42	8.10,7.30,6.80,9.80 (s,OH)	8.19,7.36,6.90,10.05 (s,OH)	0.09,0.06,0.10,0.25
2-Hydroxynaphthalene	8.46	- 0.46	8.15,7.32,6.82,10.05 (s,OH)	8.2,7.42,6.95,10.20 (s,OH)	0.05,0.10,0.13,0.15
1,5-Dihydroxynaphthalene	8.68	- 0.24	7.61 (d,2H),7.25(t,2H) 6.73(d,2H),10.20(s,OH)	7.70 (d,2H), 7.31 (t,2H) 6.82(d,2H),10.25(2,OH)	0.11,0.06,0.09,0.05

(Continued.....)

(Table 2. Continue)

2-Hydroxy-1-naphthaldehyde	8.38 - 0.54	7.40,7.35,10.42(s,OH), 8.79(s,CHO)	7.50,7.42,10.58(s,OH), 8.99(s,CHO)	0.10,0.07,0.16,0.20
2-Hydroxy-1-nitrosophthalene	8.49 - 0.43	7.49,7.35,10.12(s,OH)	7.60,7.54,10.22(s,OH)	0.11,0.10,0.10
Acenaphthene	8.41 - 0.51	7.39,7.18,3.01(s, 2CH ₂)	7.50,7.25,3.12(s,2CH ₂)	0.11,0.07,0.11
<i>Naphthalene P.T. complexes</i>				
1-Naphthylamine	8.46 - 0.46	8.11,7.72,7.35,5.65(s,NH ₂)	8.22,7.81,7.38,6.33 (NH ₃)	0.11,0.09,0.03,0.68
2-Naphthylamine	8.50 - 0.42	8.00,7.65,7.42,5.70(s,NH ₂)	8.10,7.70,7.38,6.40 (NH ₃)	0.10,0.05,0.04,0.70
<i>Phenanthrene C.T. complexes</i>				
Phenanthrene	8.63 - 0.29	8.42,7.50	8.56,7.60	0.14,0.10
9-Bromophenanthrene	8.79 - 0.13	8.01,7.81	8.12,7.92	0.11,0.11

Signal of picric acid (free) 8.92

^a θ y in ppm., solus, in DMSO-d₆.

which causes a higher deshielding for their protons.

(ii) In the other class of complexes, i.e. C.T. type, the signals of the aromatic ring protons of the donor molecule are shifted down fields while those of the acceptor display an opposite shift.

(III) ¹³Cnmr Spectra. To throw more light on these types of interactions, ¹³Cnmr spectra of the above picrates were investigated and proved to be a very useful tool in determining the type of charge transfer complex.

In both cases of interaction, the carbon signals of the carbon skeleton of picric acid will undergo different chemical shifts and hence resonate at values different from those of the free acid. The magnitude of the shifts is dependent on the type and strength of interaction.

¹³Cnmr of free picric acid I and its dissociated form II were calculated [10] and compared with experimental findings (c.f. Table 3). The observed chemical shifts of the carbons of picric acid as well as the naphthalene or phenanthrene moieties in the C.T. complexes under investigation were recorded in Table 4.

The change in the ¹³Cnmr chemical shifts for each carbon (especially C-1 since it is directly attached to the O-H or the O groups) could be taken as a measure of the type of interaction taking place in these classes of compounds.

In the case of the complexes of the salt type, the negative charge on the phenoxide is greatly delocalized by resonance through the trinitrophenyl ring causing a change in the chemical shift of C-1 by about 13 ppm (c.f. Table 4). Carbons 3 and 5 of the acceptor (picric acid) molecule did not show any considerable sign of the effect, while carbon 2 and 6 showed to be affected differently. This was expected due to steric interactions occurring in the bonded nitro groups.

In the ¹³Cnmr spectra of the complexes of the molecular type C-1 resonated at δ 153.34-157.27 (Table 4). Thus a C.T. formation must be playing a dominate role in the formation of the addition compound of this class

Table 3. ¹³C-Chemical shifts of picric acid^a

Carbon assignment	Calculated	Experimental
1	150.5 163.5	156.4
2,6	137.0 141.5	137.0
3,5	125.3 126.1	125.3
4	142.4 136.0	142.4

^a δ in ppm. solns. in DMSO-d₆

Table 4. ¹³C Nmr spectral data of C.T. complexes^a

Donor	Picric acid moiety				Naphthalene or phenanthrene moiety	Others
	C-1	C-2,6	C-3,5	C-4		
Naphthalene	157.07	137.63	125.79	141.64	129.10,128.24,126.43	
1-Bromonaphthalene	156.48	131.99	125.49	141.70	130.64,129.76,128.13,127.72,125.21, 123.21,121.05	
1-Chloronaphthalene	155.16	133.87	125.08	140.18	134.27,129.89,128.24,127.66,127.25, 126.78,126.08,125.85,123.80	
1-Methylnaphthalene	156.31	133.86	125.73	141.47	135.85,131.93,129.59,128.89,128.65, 128.07,127.60,126.49,126.14,124.44	21.83(CH ₃) (Butyl)

(Continued.....)

(Table 4 Continue)

1-Butylnaphthalene	155.49	133.98	125.73	141.58	139.01,131.93,129.00,126.66,126.25, 126.02,125.90,124.09	33.18,32.59,22.88, (Butyl)
3,6-Dimethylnaphthalene	157.49	135.38	125.49	141.79	135.38,128.36,127.54,127.42,126.72, 126.20	21.54(CH ₃)
1-Acetonaphthalene	157.27	135.09	125.49	141.64	133.80,133.04,129.76,129.41,128.71, 128.07,127.19,126.55,125.79,124.97	201.84(CO),30.08 (CH ₃)
Naphthalene-1-carboxaldehyde	156.31	133.86	125.79	141.47	137.19,135.67,131.40,130.35,129.54, 129.41,129.18,122.37,124.73	194.47(CO)
1-Hydroxynaphthalene	153.58	134.74	125.50	140.94	158.73,127.60,126.66,126.31,124.97, 124.73,122.39,118.71,108.47	
2-Hydroxynaphthalene	153.58	134.74	125.50	140.94	158.90,129.71,128.54,128.30,128.01, 126.55,123.15,119.18,109.29	
1,5-Dihydroxynaphthalene	153.34		125.67	141.70	159.43,127.48,126.43,125.20,113.15, 108.82	
2-Hydroxy-1-naphthaldehyde	157.07	132.34	125.67	141.58	164.40,138.83,129.53,129.24,128.13, 127.95,124.62,121.87,119.12,112.57, 145.85,131.40,128.07,126.43,122.22, 119.41	193.59(CO)
Acenaphthene	157.12	133.86	125.40	141.76	128.51,128.79,127.80,127.92,126.61, 125.28,121.63,121.11	30.08(CH ₂)
1-Naphthylamine	163.15	133.80	125.35	141.87	128.56,128.70,127.75,127.60,126.68, 126.40,125.00,121.66,120.80	
2-Naphthylamine	162.85	133.61	125.40	141.75	130.06,128.77,127.60,127.07,123.04	
Phenanthrene	157.25	131.93	125.61	141.64	131.64,130.35,128.89,128.59,128.07, 127.31,126.90,126.66,122.34	
9-Bromophenanthrene	156.72	134.74	125.67	141.58		

a δ in ppm, Solns. in DMSO-d₆

of compounds. However, no significant changes were observed for the other carbons of picric acid skeleton in this specific example.

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