

DIPOLE MOMENTS AND MOLECULAR STRUCTURE OF PICRATES OF AROMATIC HYDROCARBONS AND HETEROCYCLIC AMINES

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INTRODUCTION

A GREAT number of typical molecular compounds belong to the group of complexes formed of molecules, in the formation of which no atoms are transferred but in a certain measure a transfer of electrons takes place. Such compounds with different donor acceptor types in which the original molecules associate in a definite ratio have been described in a classical review by Pfeiffer²⁴ and in recent literature.^{3, 13, 33} Considerable attention has been given to various physical methods which have been successfully applied to show the existence and to study their properties like equilibrium constants,^{16, 26} heats of formation and other thermochemical data,^{3,4} melting point elevation,²⁷ magnetic susceptibilities,¹² optical constants,²¹ viscosity³ and X-ray, infra-red, etc., data.^{8, 11} Information regarding the nature of the binding forces in such compounds as derived from a study of electric polarization and dipole moments have also been recorded.^{3, 6, 14, 15, 28, 30}

A large number of hydrocarbon, ether, phenol, amine oxide, and other closely related derivatives of polynitro-compounds can be obtained in crystalline form and belong to the class of non-salt-like compounds. The polynitro-compound complexes have been the subject of many investigations.^{2, 7, 18, 25, 32} However, these have not brought any fundamental clarification of the physical origin of the absorption bands characteristic of these molecular complexes.^{19, 20, 22} Though the possibility of a clarification of the binding in molecular compounds under the assumption of an electron transfer mechanism between the donor and acceptor components of the molecular complex has been put forth by various authors^{5, 31} the quantum mechanical quantitative formulation was due to Mulliken.^{19, 20} Dipole moment measurements have been made in the case of a few aromatic hydrocarbon picrates and discussed in terms of the integrated theory of Mulliken.

Measurements have also been extended to include a few salt-like heterocyclic amine picrates.

EXPERIMENTAL

Materials and Their Purification

Aromatic hydrocarbon picrates.—Naphthalene and acenaphthene picrates were obtained from alcoholic solutions, while phenanthrene picrate from benzene solution. All three picrates were recrystallised from ethyl alcohol.

Naphthalene picrate: Yellow needles, melting point 149° C.

Acenaphthene picrate: Orange needles, melting point 162° C.

Phenanthrene picrate: Orange brown needles, melting point 162° C.

Heterocyclic amine picrates.—All the heterocyclic amines were used in alcoholic solutions.

Pyridine picrate, recrystallised from alcohol thrice, melting point 164° C.

Piperidine picrate, recrystallised from water and dried *in vacuo*. Yellow stout needles, melting point 151° C.

α -Picoline picrate, recrystallised from water and dried *in vacuo*. Yellow stout crystals, melting point 169° C.

β - and γ -Picoline picrates—Both recrystallised from alcohol. Puffy needles, melting points 170° C. and 168° C. respectively.

Quinoline picrate, recrystallised from dioxan, melting point 202° C.

Isoquinoline picrate, recrystallised from large volume of alcohol, yellowish needles, melting point 221° C.

Apparatus and Methods of Measurement

Details of the apparatus and methods of measurement of dielectric constants and densities have been given in an earlier paper.²⁹ The same procedure has been adopted for the evaluation of dipole moments.

DISCUSSION

Aromatic hydrocarbon picrates.—Mulliken has classified the hydrocarbon picrates as belonging to the neutral even system containing easily ionized bonding π electrons ($b \pi_a$) plus neutral even system containing relatively strongly held π electrons ($x \pi_a$) type. Evidence for characterising these as

TABLE I

Temperature $35^{\circ} \pm 0.01^{\circ} \text{C}$.

Solvent: Dioxan

Mole fraction	Dielectric constant	Density
Naphthalene picrate		
0.001112	2.20818	1.01805
0.002699	2.22146	1.01980
0.004200	2.23143	1.02150
0.004609	2.33540	1.02199
0.003818	2.22871	1.02122
Acenaphthene picrate		
0.001321	2.20661	1.01840
0.003126	2.22143	1.02067
0.001889	2.21085	1.01908
0.001914	2.21145	1.01911
Phenanthrene picrate		
0.000398	2.19603	1.01732
0.000551	2.19754	1.01751
0.001578	2.21115	1.01889
0.001615	2.21175	1.01893
Pyridine picrate		
0.000158	2.21965	1.01805
0.000396	2.24255	1.01832
0.000560	2.26147	1.01857
0.001115	2.31822	1.01926
0.001765	2.39289	1.02000
Piperidine picrate		
0.001216	2.37994	1.01934
0.001970	2.45661	1.02006
0.003625	2.62686	1.02198
0.004998	2.75330	1.02350

TABLE I (Contd.)

Mole fraction	Dielectric constant	Density
α -Picoline picrate		
0.000039	2.22156	1.01878
0.000282	2.25000	1.01910
0.000607	2.28742	1.01958
0.000789	2.31138	1.01983
0.001115	2.34930	1.02030
β -Picoline picrate		
0.000113	2.22255	1.01904
0.000200	2.23300	1.01914
0.000591	2.28360	1.01961
0.000800	2.31138	1.01986
γ -Picoline picrate		
0.000101	2.22958	1.01723
0.000273	2.25156	1.01743
0.000509	2.28156	1.01780
0.000941	2.33654	1.01833
Quinoline picrate		
0.000059	2.20296	1.01690
0.000130	2.20931	1.01698
0.000217	2.21687	1.01708
0.000070	2.20386	1.01692
Iso-quinoline picrate		
0.000031	2.22458	1.01720
0.000108	2.23160	1.01730
0.000150	2.23658	1.01736
0.000262	2.24657	1.01750

TABLE II

		Naphthalene picrate	Acenaphthene picrate	Phenanthrene picrate
Hedestrand α	..	3.28	3.62	6.04
Hedestrand β	..	1.125	1.18	1.246
Molar refraction (cm. ³)*	..	88.48	95.66	103.96
Total polarisation (cm. ³)	..	182.34	195.52	278.91
Orientation polarisation (cm. ³)	..	93.86	99.86	174.95
Dipole moment (D)	..	2.18	2.25	2.97

* Calculated from bond refractions given by Denbigh (see Ref. 29).

members of the above type is due to the fact that a strong charge-transfer absorption maximum is observed in the case of naphthalene picrate.²⁶ The following assumptions are made in the application of the charge transfer scheme of Mulliken: (i) The molecular components try to combine so that the polarization and dispersion forces are possibly large and consequently the planar rings of picric acid and the hydrocarbon must lie parallel with mutual approximately symmetrical axis passing through the plane of the rings. (ii) The charge transfer co-ordinate does not much deviate from the line perpendicular to the two rings. (iii) The interplanar distance has been assumed to be 3.2 Å as has been fixed by Briegleb and Czekalla⁶ for the chloranil hexamethyl benzene complex. (iv) The ionic character has been calculated assuming that the component of the moment of picric acid along the charge transfer co-ordinate is small and hence neglected.

According to the theory of Mulliken, from the known values of S , μ_1 (the ionic moment), μ_0 (the covalent moment) and μ_N (experimental moment), the coefficients a and b as well as the ratio $b^2/(a^2 + b^2)$ corresponding to the ionic character has been calculated and recorded in Table IV.

The $b \pi_a + x \pi_a$ complexes of aromatic hydrocarbons with polynitro-compounds like picric acid involve partially localised donor-acceptor interaction similar to that postulated by Abrahams.¹ In fact for such 1:1 complexes between aromatic or unsaturated π donor and π acceptors of the aromatic polynitro-compound type, Mulliken's theory predicts that the electric vector should be polarised with a large component perpendicular to the

TABLE III

	Pyridine picrate	Piperidine picrate	α -Picoline picrate	β -Picoline picrate	γ -Picoline picrate	Quinoline picrate	Isoquinoline picrate
Hedstrand α	.. 46.31	45.51	52.89	56.16	56.77	40.88	42.56
Hedstrand β	.. 1.238	1.114	1.362	1.130	1.251	1.112	1.253
Molar refraction (cm. ³)*	72.75	75.11	77.40	77.40	77.40	88.29	88.29
Total polarisation (cm. ³)	1568.75	1534.38	1768.16	1879.44	1898.29	1329.36	1449.27
Orientation polarisation (cm. ³)	1496.00	1459.27	1690.76	1802.04	1820.89	1241.07	1360.98
Dipole moment (D)	.. 8.70	8.59	9.25	9.55	9.60	7.92	8.30

* Calculated from bond refractions of Denbigh (see Reference 29).

TABLE IV*

Molecular compound	Moment of the hydrocarbon	Moment of the complex	a	$b\ddagger$	$b^2/(a^2+b^2)$
Naphthalene picrate ..	0.00	2.18	0.9109	0.3304	0.117
Acenaphthene picrate	0.97	2.25	0.9039	0.3362	0.122
Phenanthrene picrate ..	0.00	2.97	0.8811	0.39380	0.166

* The value of overlap integral S is taken to be 0.1 as assumed by Mulliken.

$$\mu_1 = e \times 3.2 \text{ \AA} = 15.3 \text{ D and } \mu_0 = 0.$$

† Mainly because of its strong dependence on the uncertain quantity S the value of b can only be relative.

TABLE V*

Picrate	Moment of the base	Covalent moment μ_0	Moment of the complex	a	$b\ddagger$	$b^2/(a^2+b^2)$
Pyridine ..	2.21	2.257	8.70	0.7036	0.6982	0.496
Piperidine ..	1.17	1.625	8.59	0.6920	0.7092	0.512
α -Picoline ..	1.72	1.914	9.25	0.6644	0.7355	0.551
β -Picoline ..	2.30	2.325	9.55	0.6584	0.7411	0.559
γ -Picoline ..	2.57	2.539	9.60	0.6609	0.7389	0.556
Quinoline ..	2.18	2.235	7.92	0.7434	0.6557	0.438
Isoquinoline ..	2.52	2.498	8.30	0.7316	0.6686	0.455

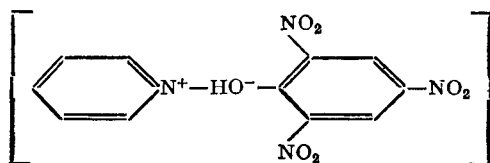
* Resultant of picric acid 1.57 D^{17} was taken as acting at an angle of 71° to the C-O bond. This angle was derived from the bond moment values of 0.8 D for the C-O link and 1.51 D for the H-O link, from which and a resultant moment of 1.51 D , an angle of 101° was obtained for the C $\ddot{\text{O}}$ H. In all the heterocyclic amines the resultant moments were assumed to act from nitrogen towards the ring²³. R_{ab} employed in the above calculations was taken from N-O distance in hydroxylamine hydrochloride.¹⁰

$\mu_1 = 4.803 \times 3.22 \text{ \AA} = 15.46 \text{ D}$. $S = 0.0177$ calculated from S_{ab} Slater overlap integral using Slater μ values for N^+O^- ions.²¹

† Mainly because of its strong dependence on the uncertain quantity S the value of b can only be relative.

planes of the two interacting molecules which are parallel to each other. In such cases of closed shell donors and acceptors, when a donor and the acceptor come into close proximity, the initial no-bond function ψ_0 (D.A) becomes increasingly admixed with a dative function ψ (D^+A^-). Though ψ_0 would result in a steady rise in exchange repulsion for increasingly close approach^{19, 20} a charge transfer outer complex can be formed, the corresponding repulsion energy rise being overcome by resonance between ψ_0 and ψ_1 .

Heterocyclic amine picrates.—In the following structure given for the ionic but indissociated reaction product



C will be only slightly larger than zero. If C is increased the hydrogen atom moves towards the nitrogen with the consequent tendency for Sp^3 hybridization. In the ultimate analysis, the U (C) curves for the complexes of the heterocyclic amine picrate type ($n + h\sigma_d$), should probably have a shallow minimum showing an inner complex corresponding to ($C = 1$), $b^2 \approx a^2$ and an activated complex ($C=0.5$) (Table V). The variation of ionic character values $b^2/(a^2 + b^2)$ from 0.559 for β -picoline picrate to 0.438 for quinoline picrate shows that the structure of the picrates varies in between an inner complex with maximum transfer and an activated complex, the individual salt molecules being stable in dioxan solutions.

SUMMARY

Dipole moment measurements have been made in the case of a few aromatic hydrocarbon picrates, the values obtained being 2.18, 2.25, 2.97 (all in Debye units) for picrates of naphthalene, acenaphthene and phenanthrene respectively and the results discussed in terms of Mulliken's theory. Measurements have also been extended to include a few salt-like heterocyclic amine picrates.

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