ANALYSIS OF THE PARTICIPATION OF *n*-π and π-π ISOMERIC COMPLEXES IN COMPLEXATION OF AZA-AROMATIC COMPOUNDS WITH 1,3,5-TRINITROBENZENE

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A simple mathematical treatment is derived allowing extraction of separate complexation constants for *n*-π and π-π isomeric complexes of aza-aromatic compounds with the acceptor 1,3,5-trinitrobenzene. The interactions between donor and acceptor in *n*-π complex follow simple concepts of steric accessibility, while the interaction in π-π complex parallel those of the parent deaza-compounds.

With aza-aromatic compounds derived from alternant hydrocarbones, molecular complexes with electron acceptors could involve participation of the *n*-π and π-π isomeric complexes. Although this possibility is well established (for citations of various discussions, see, *e.g.*, Foster and Morris[1]), there are no recorded attempts at quantitative elucidation of the contributions of each possible type of complexation to the observed complexation constants. This paper attempts a separation of this type for the corresponding complexes of methylpyridines and quinolines.

EXPERIMENTAL

For the details of the method see, *e.g.*, ref.[2]. By NMR technique, using a Varian A-60 D spectrometer (probe temperature 37°C), we established complexation constants and complexation shifts for complexes of 1,3,5-trinitrobenzene with naphthalene, 2-methylnaphthalene, phenanthrene and 1-azaphenanthrene. The concentration of donors ranged from 0·05 till 0·8 mol kg^{-1} and that of acceptor was taken equal to 0·01 mol kg^{-1} and kept constant. These complexes were studied for having more complete data to discuss *n*-π and π-π participation.

RESULTS AND DISCUSSION

Algebraic treatment of complexation involving n-π *and* π-π *isomeric complexes.* We assume the following equilibria:

$$A + D \xrightleftharpoons{K_1} C_1 \; ; \quad A + D \xrightleftharpoons{K_2} C_2 , \qquad (1), (2)$$
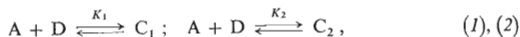
where A, D, C_1, and C_2 are the respective concentrations of acceptor, donor, n-π complex, and π-π complex, and K_1 and K_2 are the relevant complexation constants.

Now if the chemical shifts of acceptor protons in each of the two types of complexes were directly accessible, equations (3) and (4) would hold:

$$C_1 = (\Delta_1/\Delta_1^0)\, A_0\,, \quad C_2 = (\Delta_2/\Delta_2^0)\, A_0 \qquad (3),(4)$$

where Δ_1 is the complexation shift of acceptor protons at concentration of n-π complex equal to C_1 and Δ_1^0 the corresponding complexation shift for pure n-π complex and A_0 is initial concentration of acceptor; the complexation shift for pure complex is defined as a difference between chemical shift of acceptor protons in free molecule and that in pure complex; Δ_2 and Δ_2^0 are the analogous terms for the π-π complex. However, the observable shifts on complexation (Δ) are contributed to by both types of complexes and for fast equilibrium the following equation is valid:

$$\Delta = (\Delta_1^0 C_1 + \Delta_2^0 C_2)/A_0\,. \qquad (5)$$

This equation together with the definitions for K_1 and K_2 leads to equation

$$\Delta/D + \Delta(K_1 + K_2) = \Delta_1^0 K_1 + \Delta_1^0 K_2\,, \qquad (6)$$

which is identical in form to the equation

$$\Delta/D + \Delta K = \Delta^\circ K\,,$$

used by Foster and Morris[1] for a simple complexation equilibrium.

It is evident that the following relationships are valid

$$K = K_1 + K_2 \quad \text{and} \quad \Delta^\circ = (\Delta^\circ K_1 + \Delta_2^0 K_2)/(K_1 + K_2)\,, \qquad (7),(8)$$

where K and Δ° are the apparent complexation constant and complexation shift respectively.

Extraction of complexation constants K_1 *and* K_2 *from observable quantities.* The following reasoning was used: The relative change in K_1 values which express the interaction between donor and acceptor in n-π complex was supposed to follow the steric accessibility of the n-electrons. Methyl groups *ortho* to nitrogen should decrease K_1 while quinoline (or 1-azaphenanthrene) and 2-methylquinoline are supposed to be roughly equivalent to pyridines with one and two *ortho*-substituents regarding steric accessibility of the n-electrons. As to the K_2 values, which express

TABLE I

Observed and Calculated Complexation Constants and Complexation Shifts for Complexes with 1,3,5-Trinitrobenzene in CCl_4[a]

No	Group	Compound	Experimental		Calculated		Experimental	
			K	K_{02}	K_1	K_2	$\Delta°$	$\Delta°_{02}$
1		pyridine	1·5[b]	0·5[c]	1·15	0·22	7[b]	76[c]
2	I	3,4-dimethylpyridine	1·9[b]	1·0[c]	1·15	0·45	17[b]	67[c]
3		3,5-dimethylpyridine	1·8[b]	1·0[c]	1·15	0·45	16[b]	65[c]
4		2-methylpyridine	1·0[b]	0·7[c]	0·83	0·31	18[b]	72[c]
5		2,3-dimethylpyridine	1·4[b]	1·0[c]	0·83	0·45	23[b]	67[c]
6		2,4-dimethylpyridine	1·4[b]	1·0[c]	0·83	0·45	21[b]	65[c]
7	II	2,5-dimethylpyridine	1·3[b]	0·9[c]	0·83	0·41	21[b]	68[c]
8		quinoline	2·7[b]	3·85	0·83	1·73	67[b]	105
9		1-azaphenanthrene	6·4	11·8	0·83	5·30	84	125
10		6-methylquinoline	3·7[b]	6·9	0·83	3·10	73[b]	100
11		2,6-dimethylpyridine	0·8[b]	1·0[c]	0·43	0·45	31[b]	65[c]
12	III	2,4,6-trimethylpyridine	1·0[b]	1·4[c]	0·43	0·63	38[b]	61[c]
13		2-methylquinoline	3·1[b]	6·9	0·43	3·10	82[b]	100
14		quinoline[d]	0·4[b]	—	—	—	120[b]	—
15		naphthalene[d]	1·1	—	—	—	—	121
16		2-methylquinoline[d]	0·5[b]	—	—	—	110[b]	—
17		6-methylquinoline[d]	0·6[b]	—	—	—	100[b]	—
18		2-methylnaphthalene[d]	1·7	—	—	—	—	109

[a] The complexation constants are expressed in kg mol^{-1} and complexation shifts in Hz. [b,c] The data are taken from refs [1] and [2] respectively, those undesignated are the authors' results. However, these results were obtained at 37° while those in refs [1] and [2] at 33·5°. [d] Deuteriochloroform used as solvent.

an interaction in π-π complex, they are assumed to be linearly related to the complexation constants for the correspondingly substituted deaza-compounds (hydrocarbons):

$$K_2 = K_{02}k . \qquad (9)$$

Coefficient k should be smaller than 1 since the substitution of nitrogen atom for carbon atom reduces the π-electron donating "power" of the donor, and, consequently, decreases the energy of π-electron MO's of the donor.

According to this reasoning the data in Table I are divided into three groups.*

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* The K values for 3- and 4-methylpyridines[1] 2·0 and 2·4 were not included since it proved quite difficult to account for their being higher when compared to K values for the corresponding di- or even trimethylpyridines[1].

For each of these groups the folloving linear correlation can be written

$$K = K_1 + K_2 = K_1 + kK_{02} \,. \tag{10}$$

The least square method gives the expressions:

group I $K = 1{\cdot}15 + 0{\cdot}7\,K_{02}\,, \quad r = 0{\cdot}970\,, \quad n = 3\,;$ (11)

group II $K = 0{\cdot}83 + 0{\cdot}46\,K_{02}\,, \quad r = 0{\cdot}996\,, \quad n = 7\,;$ (12)

group III $K = 0{\cdot}43 + 0{\cdot}40\,K_{02}\,, \quad r = 0{\cdot}999\,, \quad n = 3\,;$ (13)

where r is a correlation coefficient and n is number of points. In spite of a small number of points these results show that the complexation constants K_1 actually are in agreement with the simple concepts of steric accessibility and that the k value for each of the three groups is smaller than 1.

There is, however, no reason to assume different k values for compounds within each of the three groups. The difference between k value in equation (11) and those in equations (12) and (13) is probably due to:

a) a small number of points included in equation (11), b) relatively small K_{02} values for the compounds entering the group I, which results in a small sensitivity of K values to the change in K_{02} and, consequently, in quite a large error in establishing k value, c) the lowest value of correlation coefficient of equation (11). For further discussion
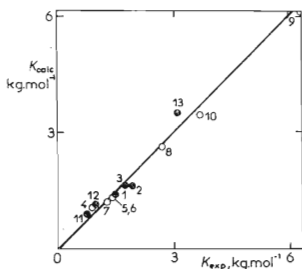

Fig. 1

Calculated *vs* Experimental Complexation Constants

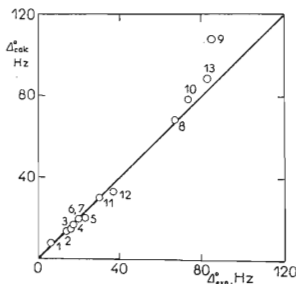● Groups I and III; ○ Group II. Numbering according to Table I.

Fig. 2

Calculated *vs* Experimental Complexation Shifts

Numbering according to Table I.

only one k value equal to 0·45 will be taken for each of the three groups. Fig. 1 shows a very close correspondence between the K values calculated by means of equation (10), using k value equal to 0·45, and the experimental data. The statistical treatment gives the following result $K_{calc} = 1·01 K_{exp} - 0·045$, $r = 0·991$, $s = 0·201$, $n = 13$, where r is the correlation coefficient, s is the standard error and n is number of points. This correspondence is regarded to be a strong support for the correct division of an interaction in the n-π and π-π isomeric complexes studied. We assume that the physically reasonable k and K_1 values do increasingly support the correctness of the present model.

Relationship between observed and calculated complexation shifts. Observed complexation shifts can be treated according to equation (8). Such a treatment may both account for the nature of Δ_1^0 and Δ_2^0 values and check the present model validity. We assume that Δ_1^0 (the complexation shift of n-π complex) can be regarded as a constant for all of the donors. There is, however, no well-grounded reason for this assumption. We simply start from the fact that, where n-π complex prevails (relatively large value of K_1) a small value of complexation shift Δ^0 is observed (Table I). This can also be rationalized basing on the geometry of the n-π complex where the planes of aromatic rings of donor and acceptor are perpendicular to each other, the ring-current effect in donor causing only a small shielding (or deshielding) of the acceptor protons. Thus, the assumption of the constancy of Δ_1^0 can also imply the fact that the Δ_1^0 values for n-π complexes of different n-donors are relatively small. On the other hand, Δ_2^0 values for the π-π complexes of aza-compounds may be put equal to the complexation shifts for the corresponding deaza-compounds (Δ_{02}^0). This assumption is based on the supposition that the geometries and the ring-current effects are approximatively equal in π-π complexes of both the aza- and the corresponding deaza-compounds. Inserting proper values in equation (8) Δ_1^0 value of -6 Hz for pyridine complex was obtained.* The pyridine complex was chosen because the n-π complexation prevails in this particular case. The value of -6 Hz was used for further calulation of the complexation shift for all other complexes with aza-compounds on the basis of equation (8). Calculated and experimental complexation shifts are plotted in Fig. 2 which shows a relatively good correspondence for all complexes except that belonging to 1-aza-phenanthrene. The statistical treatment gives

$$\Delta_{calc}^0 = 1·21 \Delta_{exp}^0 - 7·15$$

with $r = 0·989$, $s = 3·87$ and $n = 13$.

Attempts to eliminate n-π *complexation by solvent variation.* Since the assigned K_1 values for quinolines are relatively small even in tetrachloromethane. Table I

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* It is interesting but, probably, not significant that for the complex of p-benzoquinone with pyridine (in CCl_4) the value of complexation shift equal to -7 Hz was found experimentally[4].

and above discussion), we thought that a change to chloroform-d solvent, where the n-electrons of the aza-compounds would be expected to hydrogen-bond to the deuteron, would reduce K_1 to a negligible value so that the observed K would refer to pure π-π complexation. The ratio between K values for complexes of quinolines and correspondingly substituted naphthalenes in chloroform-d gives k value of 0.35 (Table I) which is close to the k value of 0.45 discussed above. A small difference can be accounted for by the effect of hydrogen bond which increases electronegativity of the nitrogen atom and, consequently, reduces the k value.

The solvent change almost eliminates Δ_1^0 from the observed Δ° because of small K_1 value (equation (8)). In chloroform-d, Δ° values for naphthalene and quinoline are virtually identical (121 and 120 Hz), as are the values for 2-methylnaphthalene, 2-methylquinoline and 6-methylquinoline (109, 110 and 100 Hz), offering further confirmation of the present model.

Concluding remarks. In spite of the success of the approach used we expect a criticism because of, at least, three reasons. At first, the present work lacks a more precise analysis as to whether the presence of termolecular complexes of the type AD_2 is possible which was, it seems, firmly established during last few years for some complexes[5−7]. Secondly the effect of nonideal behavior of the component (especially of that being in a large excess) is not taken into account[8]. Thirdly, a possible effect of the chemical reactions in electron donor–acceptor system on the measured K values was not studied in detail[9]. However, we believe that the main conclusions coming from the present model would not been affected even if such analyses were done.

REFERENCES

1. Foster R., Morris J. W.: J. Chem. Soc. (B), *1970*, 703.
2. Foster R., Fyfe C. A.: Trans. Faraday Soc. *61*, 1626 (1965).
3. Emslie P. H., Foster R., Horman I., Morris J. W., Twiselton D. R.: J. Chem. Soc. (B), *1969*, 1161.
4. Kysel O., Lynch B. M.: Unpublished results.
5. Deranleau D. A.; J. Am. Chem. Soc. *91*, 4050 (1969).
6. Dodson B., Foster R., Bright A. A. S., Foreman M. I., Gorton J.: J. Chem. Soc. (B), *1971*, 1283.
7. Trotter P. J., Yphantis D. A.: J. Phys. Chem. *74*, 1399 (1970).
8. See, *e.g.*, Hanna M. W., Rose D. G.: J. Am. Chem. Soc. *94*, 2601 (1972).
9. Kearns D. R., Gardner P., Carmody J.: J. Phys. Chem. *71*, 931 (1967).

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