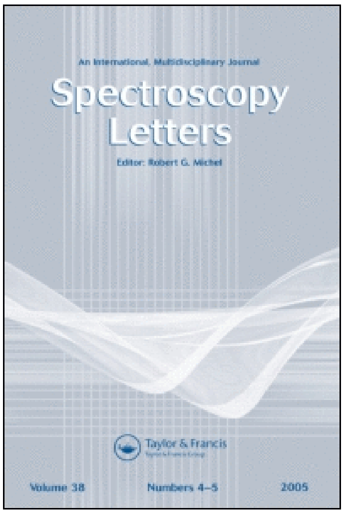

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The Influence of Substituents in Arene Ring of Aniline on Dynamic, Energetic and Electrooptical Non-equivalency of Amino Group NH-Bonds in Complexes with Intermolecular H-Bond of 1:1 and 1:2 Composition

V. E. Borisenko[a]; A. V. Morev[a]; A. A. Ponomarev[a]
[a] Department of Physics, Tyumen State University, Tyumen, Russia

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THE INFLUENCE OF SUBSTITUENTS IN ARENE RING OF ANILINE ON DYNAMIC, ENERGETIC AND ELECTROOPTICAL NON-EQUIVALENCY OF AMINO GROUP NH-BONDS IN COMPLEXES WITH INTERMOLECULAR H-BOND OF 1:1 AND 1:2 COMPOSITION

Key words: hydrogen bond, substituted anilines, dynamic and electrooptical amino group parameters, energetic characteristics of H-bonded complexes

V.E.Borisenko, A.V.Morev, A.A.Ponomarev

Department of Physics, Tyumen State University
10 Semakova str., Tyumen 625000, Russia

ABSTRACT

Infrared spectra of free and bound with different proton acceptors in 1:1 and 1:2 complexes H-bonded molecules of 3,5-dichloroaniline, 3,5-dibromoaniline, 2,3,5,6-tetrafluoroaniline, 4-methoxytetrafluoroaniline, pentafluoroaniline, 4-nitro-aniline, 2,6-dichloro-4-nitroaniline, 4-nitrotetrafluoroaniline and 4-aminotetrafluoropyridine were studied in the region of stretching and deformational vibrations of amino group. Spectral characteristics of absorption bands of free and bound H-bonded molecules of substituted anilines in solutions were determined.

With regard to dynamic and electrooptical non-equivalence of amino group NH-bonds in free and bound H-bonded molecules of anilines the solution of vibrational and electrooptical tasks was found. The valent angles γ(HNH) and the dynamic and electrooptical characteristics of amino group NH-bonds were determined. Equilibrium constants monomer-complex were calculated for 1:1 H-bonded complexes. The influence of the position, number and individual properties of substituents on donor features in H-bond, the geometrical, dynamic, electrooptical and energetic characteristics of amino group NH-bonds of anilines in complexes of different composition were investigated.

It was shown that amino group NH-bonds in 1:1 and 1:2 complexes were non-equivalent dynamically, electrooptically and energetically. Non-equivalence of NH-bonds was mainly determined by the position, number and individual properties of substituents in aniline arene ring.

The correlations between the spectral, geometrical, dynamic and electrooptical characteristics of amino group in 1:1 and 1:2 H-bonded complexes were stated.

INTRODUCTION

In earlier works [1,2] the influence of substituents (CH_3, F, Cl, Br) position in arene ring of monosubstituted anilines on geometrical, dynamic and electrooptical features of amino group in free molecules and in complexes with intermolecular H-bond of 1:1 and1:2 composition was reported.

The transition from free aniline molecules in CCl_4 to those bound into 1:2 complexes was found to be accompanied by significant increase of valent angle γ(HNH), the same effect being observed with strengthening H-bond.

Dynamic and electrooptical non-equivalence of bonded NH-groups of monosubstituted anilines in 1:1 and 1:2 complexes was studied.

The character of the dependence of amino group dynamic and electrooptical properties in complexes of various compositions on individual proton acceptors abilities was investigated.

The parameters of linear regression equations revealling interrelation of geometrical, dynamic, electrooptical and spectral features of monosubstituted H-bonded anilines were determined.

Electrooptical characteristics of amino group $\partial\mu/\partial q$ (the derivative of dipole moment with respect to bond length) and $\partial\mu/\partial q'$ (the derivative of dipole moment with respect to adjacent bond) for monosubstituted anilines were proved to depend essentially on the type and the position of substituent in aniline arene ring and on individual properties of proton acceptors.

The goal of present work is to study the influence of the number, the position and individual properties of substituents on geometrical, dynamic, energetic and electrooptical characteristics of amino group in intermolecular H-bonded complexes of anilines with various proton acceptors.

EXPERIMENT AND CALCULATIONS

Infrared spectra of H-bonded (1:2) complexes of 3,5-dichloroaniline (I), 3,5-dibromoaniline (II), tetrafluoroaniline (III), 4-methoxytetrafluoroaniline (IV), pentafluoroaniline (V), 4-nitroaniline (VI), 2,6-dichloro-4-nitroaniline (VII), 4-nitrotetrafluoroaniline (VIII) and 4-aminotetrafluoropyridine (IX) were studied in the region of stretching (3100-3600 cm^{-1}) and deformational (1550-1800 cm^{-1}) vibrations of amino group. As proton accepting solvents acetonitrile, dioxane, tetrahydrofurane (THF), dimethylformamide (DMF), dimethylsulphoxide (DMSO) and hexamethylphosphoramide (HMPA) were used, their proton accepting abilities increasing in the order of enumeration.

Infrared spectra, dynamic and electrooptical properties of amino group NH-bonds of analogous 1:1 complexes in CCl_4 were reported in [3] for I, in [4] for III, VIII, in [5] for IV, V, IX and in [6] for VI, VII. Similar investigations for 1:1 complexes of II with various proton acceptors and for 1:1 complexes of III-IX with dioxane were done in present work. Also for I spectral moments $M_c^{(1)}$ and "effective half-widths"$2(M^{(2)})^{1/2}$ of absorption bands $\nu_c(NH)$ of H-bonded 1:1

complexes with different proton acceptors were determined, those being absent in [3]. Spectral characteristics of absorption bands ν_c(NH), ν_f(NH) and equilibrium constants monomer-complex (1:1) are listed in Tables 1,2.

Infrared spectra of compounds under investigation were registered by *Specord 75 IR* instrument (Karl Zeiss Iena). Spectrogramms recording was carried out under optimum registration conditions, those were, appropriate choice of slit programm, spectrum scanning speed and time constant of the device. Necessary photometric accuracy was reached by matching absorption layer width. When studying spectra of 1:1 complexes of substituted anilines with various proton acceptors in CCl_4 disassembling cells of layer width about 4 mm were used. For spectra registrations of 1:2 complexes in aprotic solvents standart cells with constant width d=0.1-1.0 mm and glasses made from NaCl, KBr, CaF_2 were applied.

The solutions for investigations were prepared in pycnometers graduated with distilled water at room temperature.

All experiments were repeated no less than 5 times.

The technique of determining amino group spectral characteristics under conditions of monomers and complexes bands overlapping and also the solution of vibrational and electrooptical tasks within the framework of R-NH_2 model with regard to dynamic and electrooptical non-equivalence of NH-bonds in 1:1 complexes were described in detail in [2,7].

Spectral moments $M^{(1)}$ (gravity centre of the band) for absorption bands of stretching vibrations of amino groups in free molecules of substituted anilines in CCl_4 were determined to ±2 cm^{-1}, integral intensities Bm were measured with an accuracy of 5%. For complexes of 1:1 and 1:2 composition spectral moments $M^{(1)}$ of absorption bands of amino group stretching vibrations agreed within 5 cm^{-1}, integral intensities Bc were good to 10%.

Positions of absorption bands of deformational vibrations γ(HNH) of 1:1 complexes were determined within a precision of 3 cm^{-1}.

Spectral features of amino group absorption bands in complexes 1:2 are given in Table 3.

TABLE 1

The absorption band parameters of aminogroup stretching vibrations of substituted anilines in 1:1 H-bonded complexes with different proton acceptors in CCl_4

Proton donor	Proton acceptor	$\nu_f(NH)$		$\nu_c(NH)$			$K_{25°C}$
		ν_f (cm^{-1})	$B_f \cdot 10^{-3}$ ($dm^3M^{-1}cm^{-2}$)	$M_c^{(1)}$ (cm^{-1})	$2(M^{(2)})^{1/2}$ (cm^{-1})	$B^c \cdot 10^{-3}$ ($dm^3M^{-1}cm^{-2}$)	(dm^3M^{-1})
3,5-dichloroaniline (I)	Dioxane	3485	6.15	3337	117	20.3	1.33
	THF	3484	5.83	3330	117	21.1	1.53
	DMF	3485	5.79	3316	131	23.9	10.3
	DMSO	3483	4.65	3294	133	31.8	12.9
	HMPA	3482	4.46	3257	128	38.4	60.9
3,5-dibromoaniline (II)	Dioxane	3482	6.46	3331	122	20.5	1.55
	THF	3480	6.79	3323	118	26.8	1.71
	DMF	3481	6.38	3321	121	29.2	11.0
	DMSO	3478	6.02	3296	122	47.7	15.1
	HMPA	3473	5.82	3244	126	58.1	86.8

TABLE 2

The absorption band parameters of aminogroup stretching vibrations of substituted anilines in 1:1 H-bonded complexes in CCl_4 with dioxane

Substituted anilines	ν_f(NH)		ν_c(NH)			$K_{25°C}$
	ν_f (cm^{-1})	$B_f \cdot 10^{-3}$ ($dm^3M^{-1}cm^{-2}$)	$M_c^{(1)}$ (cm^{-1})	$2(M^{(2)})^{1/2}$ (cm^{-1})	$B^c \cdot 10^{-3}$ ($dm^3M^{-1}cm^{-2}$)	(dm^3M^{-1})
2,3,5,6-tetrafluoro-aniline (III)	3484	6.64	3314	126	29.3	1.29
	3490	7.28	3310	124	31.7	0.82
4-methoxytetra-fluoroaniline (IV)	3498	5.24	3307	121	31.6	1.14
pentafluoroaniline (V)						
	3492	8.59	3333	123	44.7	0.97
4-nitroaniline (VI)						
	3493	9.30	3323	118	52.4	0.61
2,6-dichloro-4-nitro-aniline (VII)	3491	9.94	3287	138	63.3	2.05
4-nitrotetrafluoro-aniline (VIII)	3492	7.81	3290	127	52.4	1.85
4-aminotetrafluoro-pyridine (IX)						

TABLE 3

The absorption band parameters of aminogroup stretching vibrations of substituted anilines in 1:2 H-bonded complexes with different proton acceptors

Studied compound	Solvent	$\nu_c^s(NH_2)$			$\nu_c^{as}(NH_2)$			$\gamma(HNH)$
		$M_s^{(1)}$ (cm^{-1})	$2(M_s^{(2)})^{1/2}$ (cm^{-1})	B_c^s ($10^3dm^3M^{-1}cm^{-2}$)	$M_{as}^{(1)}$ (cm^{-1})	$2(M_{as}^{(2)})^{1/2}$ (cm^{-1})	B_c^{as} (10^3 $dm^3M^{-1}cm^{-2}$)	(cm^{-1})
3,5-dichloroaniline (I)	1. CCl_4	3406	20	4.86	3496	27	3.87	1615
	2. CH_3CN	3342	48	30.0	3468	52	14.6	1630
	3. Dioxane	3318	117	35.1	3446	61	18.7	1632
	4. THF	3302	118	47.4	3436	85	29.2	1640
	5. DMF	3286	129	59.5	3423	91	33.7	1646
	6. DMSO	3245	144	75.8	3398	98	40.2	1646
	7. HMPA			strong overlapping of bands				
3,5-dibromoaniline (II)	8. CCl_4	3404	26	6.07	3493	30	4.50	1615
	9. CH_3CN	3344	49	29.3	3467	48	14.4	1630
	10.Dioxane	3418	118	33.5	3447	64	18.0	1634
	11. THF	3300	119	52.8	3433	66	29.5	1637
	12. DMF	3289	133	72.9	3421	78	30.0	1645
	13. DMSO	3254	138	78.9	3406	103	39.2	1645
	14. HMPA			strong overlapping of bands				
2,3,5,6 -tetrafluoro-aniline (III)	15. CCl_4	3410	18	8.21	3506	24	5.91	1612
	16.CH_3CN	3335	117	44.8	3461	59	18.5	1623
	17.Dioxane	3297	120	54.3	3424	69	21.9	1628

(continued)

TABLE 3. Continued

	18. THF	3278	124	60.3	3411	75	23.6	1634
	19. DMF	3255	134	74.8	3408	76	25.3	1636
	20. DMSO			strong overlapping of bands				
	21. HMPA			strong overlapping of bands				
4-methoxytetra-fluoroaniline (IV)	22. CCl_4	3405	19	6.91	3496	28	5.41	1608
	23. CH_3CN	3331	116	40.5	3457	63	17.2	1618
	24. Dioxane	3296	118	49.5	3424	68	19.8	1625
	25. THF	3281	120	51.0	3413	79	20.8	1630
	26. DMF	3263	120	72.7	3399	79	21.1	1640
	27. DMSO			strong overlapping of bands				
	28. HMPA			strong overlapping of bands				
pentafluoro-aniline(V)	29. CCl_4	3406	17	8.18	3499	24	6.93	1610
	30. CH_3CN	3330	115	39.0	3456	69	20.2	1622
	31. Dioxane	3293	116	46.9	3422	74	20.9	1629
	32. THF	3275	112	53.9	3406	74	22.3	1635
	33. DMF	3254	124	63.5	3391	75	23.9	1645
	34. DMSO			strong overlapping of bands				
	35. HMPA			strong overlapping of bands				
4-nitroaniline (VI)	36. CCl_4	3416	22	8.81	3511	32	3.96	1619
	37. CH_3CN	3336	125	60.3	3470	56	22.2	1635
	38. Dioxane	3309	123	62.7	3442	67	23.3	1637
	39. THF	3293	123	67.4	3429	69	24.1	1642

	40. DMF	3267	133	85.8	3424	67	25.6	1654
	41. DMSO			strong overlapping of bands				
	42. HMPA			strong overlapping of bands				
2,6-dichloro-4-nitroaniline (VII)	43. CCl_4	3414	20	12.5	3520	22	7.26	1607
	44.CH_3CN	3332	118	63.2	3467	63	21.9	1622
	45.Dioxane	3294	118	66.8	3428	74	22.4	1625
	46. THF	3264	123	72.2	3398	75	24.0	1632
	47. DMF	3245	133	90.5	3393	77	25.1	1644
	48. DMSO			strong overlapping of bands				
	49. HMPA			strong overlapping of bands				
4-nitrotetra-fluoroaniline (VIII)	50. CCl_4	3419	17	14.8	3518	24	7.62	1613
	51.CH_3CN	3305	128	82.7	3442	77	31.0	1626
	52.Dioxane	3257	133	107.0	3400	90	39.7	1630
	53. THF			strong overlapping of bands				
	54. DMF			strong overlapping of bands				
	55. DMSO			strong overlapping of bands				
	56. HMPA			strong overlapping of bands				
4-amino-tetrafluoropyridine (IX)	57. CCl_4	3423	22	13.2	3523	25	8.74	1630
	58.CH_3CN	3316	122	61.8	3450	69	27.4	1646
	59.Dioxane	3263	130	74.9	3407	84	33.3	1655
	60. THF			strong overlapping of bands				
	61. DMF			strong overlapping of bands				
	62. DMSO			strong overlapping of bands				
	63. HMPA			strong overlapping of bands				

In solving vibrational task for free and H-bonded molecules rated frequencies of amino group stretching vibrations were compared with experimental values obtained for first spectral moments of corresponding bands. For more exact solution of vibrational problem the data on stretching and deformational vibrations of deuterium substituted analogues R-NHD and R-ND_2 were invoked.

RESULTS AND DISCUSSION

Fig. 1 exhibits the manifestation of H-bond in the region of stretching vibrations of 3,5-dibromo-aniline amino group in 1:1 complexes with various proton acceptors in CCl_4. These effects are sufficiently typical and have been repeatedly discussed [1-7]. In this case intensive absorption bands of symmetrical $\nu^s(NH_2)$ and antisymmetrical $\nu^{as}(NH_2)$ vibrations correspond to free molecules of I, first spectral moments of these bands are $M_s^{(1)}$=3404 cm^{-1}, $M_{as}^{(1)}$=3493 cm^{-1}.

It is pertinent to note that corresponding spectral moments of free molecules of I are 2-3 cm^{-1} higher than those of II and also possess lesser "effective half-width" $2(M^{(2)})^{1/2}$, Table 3. Integral intensities of absorption bands of amino group stretching vibrations in II are about 15-20% above that in I. These differences are most probably caused by the fact that bromine atoms in positions 3,4 have more strong inductive influence on amino group than chlorine atoms in the same positions.

From Fig. 1 it is seen that under association of II with various proton acceptors the changes of spectra in the region of amino group stretching vibrations can be observed which are qualitatively similar for all studied anilines [1-7]. Absorption band $\nu^{as}(NH_2)$ broadens as viewed from lesser wave numbers. Below band $\nu^s(NH_2)$ wide intensive band $\nu_c(NH)$ of 1:1 H-bonded complexes having doublet or triplet structure is observed. With H-bond strengthening in the row of proton acceptors: acetonitrile, dioxane, THF, DMF, DMSO, HMPA the intensity increase of absorption band of deformational vibration $\gamma(HNH)$ overtone and also

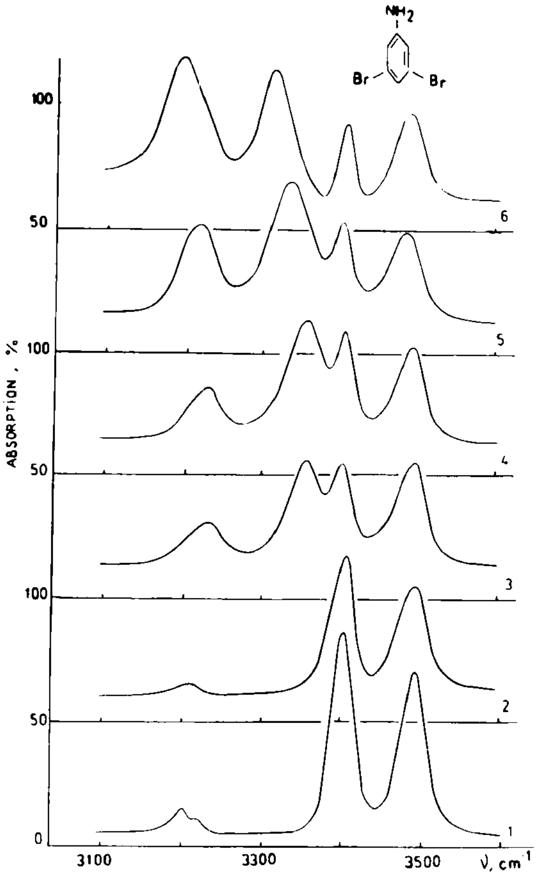

FIG. 1. The manifestation of H-bond in the region of stretching vibrations of 3,5-dibromoaniline (II) amino group in 1:1 complexes with various proton acceptors in CCl_4.
1: II (0.015 M); 2: II (0.02 M), CH_3CN (0.5 M); 3: II (0.02 M), THF (0.3 M);
4: II (0.015 M), DMF (0.1 M); 5: II (0.015 M), DMSO (0.1 M);
6: II (0.015 M), HMPA (0.03 M)

of compound vibration of arene ring located several tens cm^{-1} higher takes place. These changes are caused by Fermi resonance of vibration ν_c(NH) with 2γ(HNH) and compound frequency of arene ring.

In 1:1 complexes of II with HMPA, Fig.1, the intensity of low frequency component of Fermi resonance doublet becomes more than that of high frequency component. This results from the fact that under assotiation with the strongest proton acceptor, HMPA, the position of nonperturbed band ν_c(NH) in spectrum turns out to be lower than the position of band 2γ(HNH) [4].

Analogous spectral changes are observed in the bands of amino group stretching vibrations for I [3].

From Table 1 it follows that strengthening H-bond in 1:1 complexes leads to decreasing frequency ν_f(NH) where the main contributing component is free NH-group and to shifting spectral moment M_c to lower frequency spectral region. In this case with strengthening H-bond integral intensity Bf for I, II decreases but, however, remains higher than integral intensity of bands $\nu^s(NH_2)$ and $\nu^{as}(NH_2)$ for free molecules.

Thorough analysis of integral intensity behaviour for absorption band ν_f(NH) in 1:1 complexes can be carried out if the derivative of dipole moment with respect to normal coordinate Q_f is presented as explicit expression:

$$\left[\partial\mu/\partial Q_f\right]^2 = \left[(\partial\mu/\partial Q)^f_x\right]^2 + \left[(\partial\mu/\partial Q)^f_y\right]^2 \qquad (1)$$

for complexes of anilines with various proton acceptors. For NH_2 fragment having nonequivalent NH bonds projection of vectors of dipole moment derivatives with respect to normal coordinate Q_f onto X and Y axes $(\partial\mu/\partial Q)^f_x$ and $(\partial\mu/\partial Q)^f_y$ are complex functions of geometrical and electrooptical amino group characteristics and coefficients of normal vibrations forms [7].

Also strengthening H-bond in I,II leads to natural increase of integral intensity B_c and equilibrium constant monomer-complex, Table 1.

Relative changes of "effective half-width"$2(M_c^{(2)})^{1/2}$ in the row of proton acceptors: dioxane, THF, DMF, DMSO, HMPA are less significant.

The correlation between spectral characteristics of free and H-bonded molecules of I, II with various proton acceptors and equilibrium constants monomer-complex (1:1) enables to conclude that compound II is slightly stronger proton donor than compound I.

Fig. 2, 3 illustrate absorption bands of amino group stretching vibrations for III-IX in H-bonded (1:1 and 1:2) complexes with dioxane. One can see from these figures that spectral manifestations of complexes of different composition in the region of amino group stretching vibrations differ essentially.

In the row of proton acceptors dioxane occupies intermediate position between acetonitlrile and THF and it is the weakest proton acceptor in spectra of which under association it becomes feasible to distinguish between absorption bands $\nu_c(NH)$ of 1:1 complexes and $\nu^s(NH_2)$ of free molecules in CCl_4.

With enhacement of proton donating ability in the row of compounds I-IX the overlapping of absorption bands $\nu^{as}(NH_2)$ of free molecules with bands $\nu_f(NH)$ of 1:1 H-bonded complexes shows a decrease. Maximum position of the band $\nu_f(NH)$, Fig. 2, can be guessed in spectra ranging from compound IV and on, as proton donating abilities of substituted anilines increase. The most bands separation is observed for complexes of IX with dioxane.

Equilibrium constants for 1:1 complexes of I-IX with dioxane, Table 1, 2, are not great. The least equilibrium constant K= 0.6 dm^3 M^{-1} corresponds to complex VII-dioxane, this value being sufficiently influenced by intramolecular hydrogen bond NH ... Cl.

In high frequency spectral region of amino group stretching vibrations of 1:2 H-bonded complexes, Fig. 3, the broad band $\nu^{as}_c(NH_2)$ is observed, and below the band $\nu^s_c(NH_2)$ is placed being evident as doublet or triplet. The structure of this band as well as one of the band $\nu_c(NH)$ for 1:1 complexes has Fermi resonance nature [2]. With strengthening H-bond more and more broad overlapping of high frequency component of Fermi resonance doublet (triplet) with absorption band

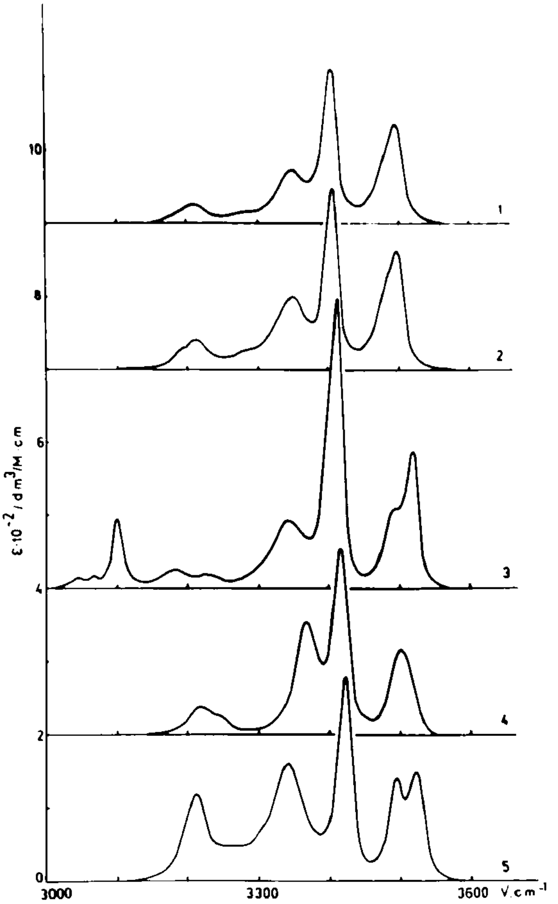

FIG.2. Absorption bands of amino group stretching vibrations ν(NH) of substituted anilines in 1:1 complexes with dioxane (C=0.3 M) in CCl_4.
1: 4-methoxytetrafluoroaniline (0.015 M); 2: pentafluoroaniline (0.015 M);
3: 2,6-dichloro-4-nitroaniline (0.005 M); 4: 4-nitroaniline (0.005 M);
5: 4-aminotetrafluoropyridine (0.011 M)

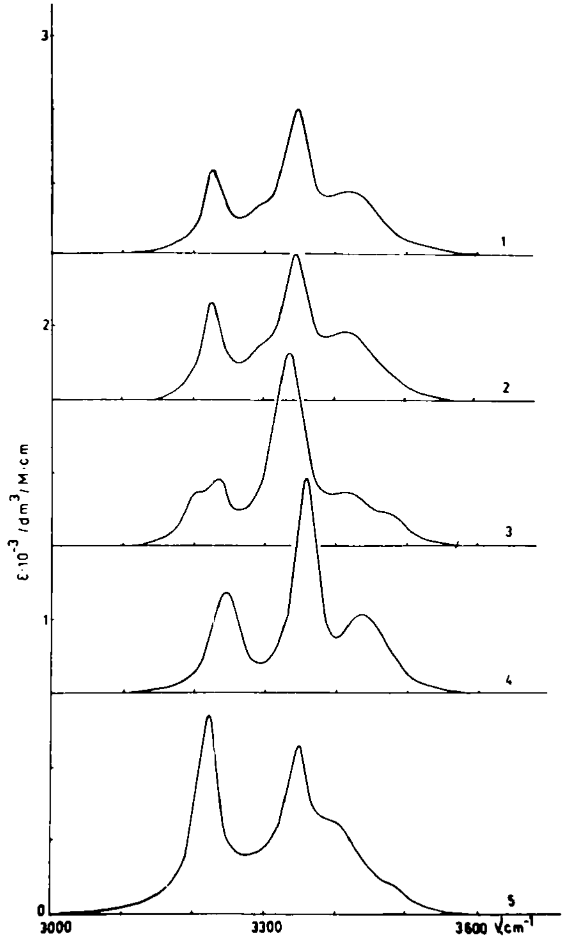

FIG. 3. Absorption bands of amino group stretching vibrations of substituted anilines in 1:2 complexes in dioxane.
1: 4-methoxytetrafluoroaniline (0.12 M); 2: pentafluoroaniline (0.12 M);
3: 2,6-dichloro-4-nitroaniline (0.12 M); 4: 4-nitroaniline (0.07 M);
5: 4-aminotetrafluoropyridine (0.11 M)

$\nu_c(NH_2)$ takes place. This adds complexity to the process of bands separation and decreases an accuracy of spectral features determining, first of all for broad and low intensive band $\nu^{as}_c(NH_2)$.

Amino group absorption bands of some other compounds in 1:2 H-bonded complexes with various proton acceptors are depicted in Fig. 4-6. It is evident from these Figures that in some cases the effect of overlapping of high frequency component of Fermi resonance band $\nu^{s}_c(NH_2)$ with the band $\nu^{as}_c(NH_2)$ is so great that the separation of these bands becomes practically impossible. For example, in spectra of compound II, Fig. 4, absorption band $\nu^{as}_c(NH_2)$ can be distinguished under association with acetonitrile, dioxane, THF, DMF, DMSO, but it isn't detecTable under association with HMPA.

For one of the strongest proton acceptors 4-nitrotetrafluoroaniline, Fig. 6, absorption band $\nu^{as}_c(NH_2)$ in 1:2 H-bonded complexes can be detected only under association with the weakest proton acceptors — acetonitrile and dioxane. These facts should be taken into account when analysing spectra of the solutions of substituted anilines in aprotic solvents in the region of amino group stretching vibrations.

From Table 3 it is obvious that the transition from free anilines molecules to 1:2 complexes is accompanied by the shift of spectral moments $M_s^{(1)}$ and $M_{as}^{(1)}$ positions to lower frequencies region and also by increase of integral intensities of absorption bands $\nu^{s}_c(NH_2)$ and $\nu^{as}_c(NH_2)$. As this takes place, relative shift of spectral moment $M_s^{(1)}$ and enhancement of integral intensity B_s of corresponding band are considerably more than those of analogous parameters $M_{as}^{(1)}$ and B_{as}.

Dynamic and electrooptical properties of amino group NH bonds for H-bonded (1:1 and 1:2) complexes of I-IX with various proton acceptors are tabulated in Table 4. The values of valent angles γ(HNH) for free molecules in CCl_4 and for H-bonded (1:2) complexes are also presented here. The data listed in Table 4 indicate that the transfer from free molecules H-bonded 1:2 complexes is followed by high increase of valent angle γ(HNH). This effect rises as proton accepting abilities of solvent strengthen.

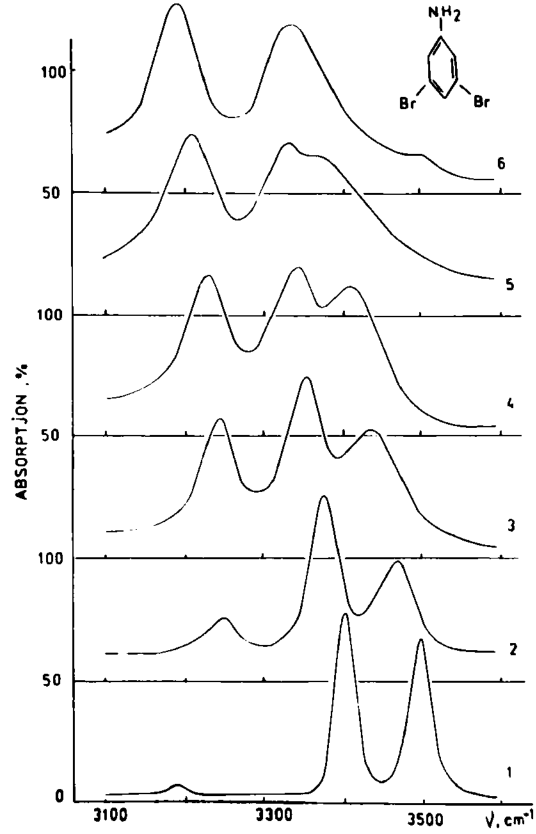

FIG. 4. The manifestation of H-bond in the region of stretching vibrations of 3,5-dibromoaniline amino group in 1:2 complexes in different solvents.
1: CCl_4 (0.015 M); 2: CH_3CN (0.15 M); 3: THF (0.15 M);
4: DMF (0.13 M); 5: DMSO (0.13 M); 6: HMPA (0.3 M)

Parameters $M_s^{(1)}$, $M_{as}^{(1)}$ and $(K(NH))^{1/2}$ of free and H-bonded (1:2) molecules are linearly dependent, Fig. 7.

For monomer molecules in CCl_4, Fig. 7 (1,2) , equations of linear regression **Y=aX+b** will look like:

$$M_{s,m}^{(1)} = 0.778(K(NH))^{1/2} + 813.2 \qquad r=0.998 \qquad (2)$$

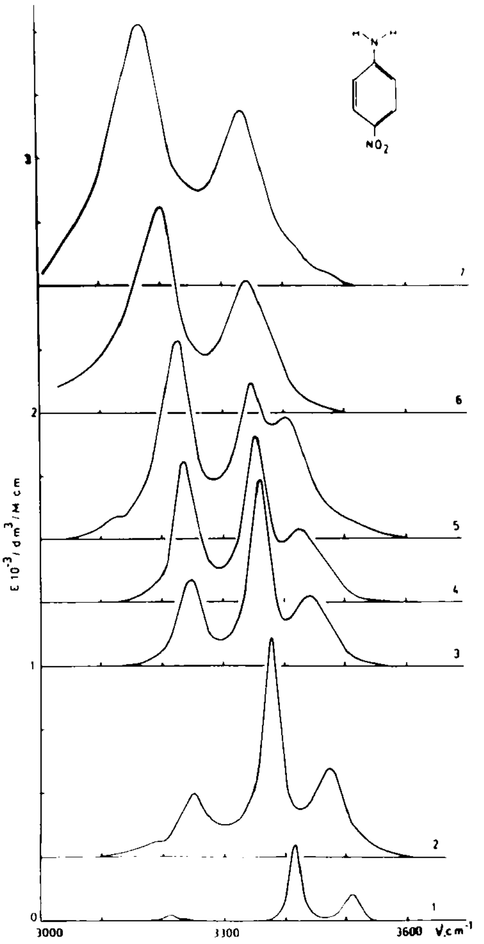

FIG. 5. The manifestation of H-bond in the region of stretching vibration of 4-nitroaniline amino group in 1:2 complexes.
1: CCl_4 (0.01 M); 2: CH_3CN (0.1 M); 3: Dioxane (0.07 M); 4: THF (0.12 M);
5: DMF (0.12 M); 6: DMSO (0.12 M); 7: HMPA (0.12 M)

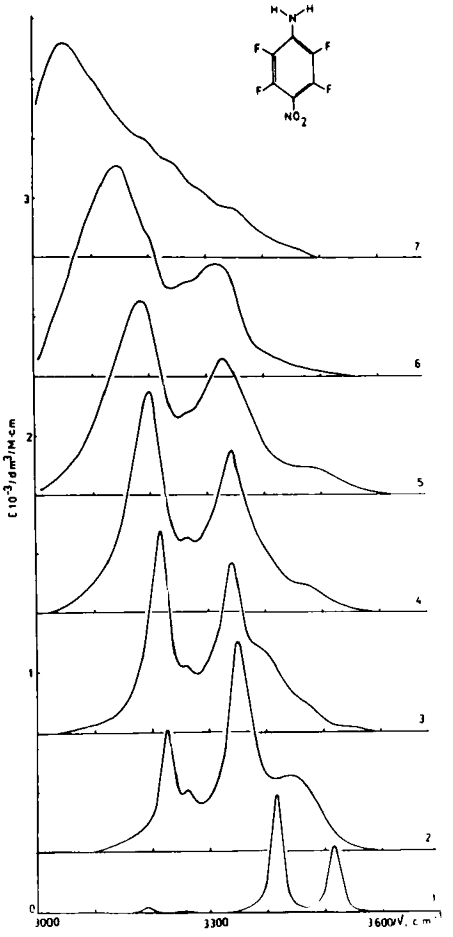

FIG. 6. The manifestation of H-bond in the region of stretching vibrations of 4-nitrotetra-fluoroaniline in 1:2 complexes in aprotic solvents.
1: CCl_4 (0.02 M); 2: CH_3CN (0.1 M); 3: Dioxane (0.12 M); 4: THF (0.12 M); 5: DMF (0.1 M); 6: DMSO (0.1 M); 7: HMPA (0.15 M)

TABLE 4

The dynamic and electro-optical characteristics of aminogroup NH bonds of subsituted anilines in 1:1 and 1:2 complexes with different proton acceptors

Studied compound	Proton acceptor	1:1 complexes					1:2 complexes				$\Delta H^1/\Delta H^2$
		$K_1(NH)$ ($10^{-6}cm^{-2}$)	$K_2(NH)$ ($10^{-6}cm^{-2}$)	$\partial\mu_1/\partial q_1$ (DA^{-1})	$\partial\mu_2/\partial q_2$ (DA^{-1})	$\partial\mu_i/\partial q_j$ (DA^{-1})	$K(NH)$ ($10^{-6}cm^{-2}$)	$\gamma(HNH)$ (deg.)	$\partial\mu/\partial q$ (DA^{-1})	$\partial\mu/\partial q'$ (DA^{-1})	
3,5-dichloro-aniline (I)	CCl_4						11.110	107.0	1.32	0.29	
	CH_3CN						10.824	117.3	3.36	1.40	
	Dioxane *	10.481	11.239	2.92	1.33	0.25	10.675	118.1	3.61	1.46	1.21
	THF *	10.433	11.238	2.95	1.28	0.34	10.595	120.1	4.38	1.71	1.04
	DMF	10.339	11.245	3.12	1.28	0.34	10.502	121.0	4.86	2.03	0.96
	DMSO	10.190	11.245	3.56	1.09	0.54	10.293	125.8	5.67	2.68	1.07
	HMPA	9.950	11.250	3.90	1.09						
3.5-dibromo-aniline (II)	CCl_4						11.096	107.0	1.45	0.34	
	CH_3CN						10.824	116.8	3.28	1.39	
	Dioxane *	10.440	11.218	2.91	1.42	0.38	10.680	118.5	3.54	1.44	1.21
	THF *	10.392	11.205	3.32	1.39	0.41	10.579	119.8	4.57	1.89	1.10
	DMF	10.376	11.218	3.44	1.31	0.49	10.507	120.0	5.09	2.42	0.95
	DMSO	10.209	11.210	4.35	1.15	0.69	10.351	126.0	5.63	2.72	1.40
	HMPA	9.872	11.195	4.70	1.23						
2,3,5,6-tetra-fluoroaniline (III)	CCl_4						11.158	108.7	1.70	0.43	
	CH_3CN	10.633	11.240	3.40	1.80	0.35	10.775	117.5	4.02	1.82	0.98
	Dioxane	10.340	11.235	3.42	1.42	0.79	10.546	118.8	4.35	2.03	1.11

	THF	10.197	11.240	4.07	1.34	0.92	10.440	120.0	4.65	2.25	1.42
	DMF	10.204	11.240	4.35	1.54	0.64	10.361	126.3	5.41	3.03	1.33
	DMSO	10.014	11.243	4.59	1.44	0.73					
	HMPA	9.692	11.258	4.61	1.40	0.89					
4-methoxy-tetrafluoro-aniline (IV)	CCl_4						11.108	107.5	1.57	0.35	
	CH_3CN	10.568	11.250	2.57	1.47	0.47	10.749	117.5	3.84	1.72	
	Dioxane	10.299	11.285	3.59	1.47	0.48	10.536	118.4	4.13	1.93	1.33
	THF	10.181	11.281	4.09	1.41	0.54	10.456	119.8	4.29	2.03	1.64
	DMF	10.173	11.294	4.44	1.61	0.31	10.356	121.3	4.88	2.68	1.45
	DMSO	10.059	11.273	4.84	1.52	0.11					
	HMPA	9.768	11.265	5.90		0.14					
pentafluoro-aniline (V)	CCl_4						11.122	108.0	1.74	0.37	
	CH_3CN	10.591	11.296	3.48	1.75	0.35	10.745	117.5	3.84	1.57	1.23
	Dioxane	10.279	11.340	3.57	1.23	1.03	10.521	118.8	4.09	1.83	1.33
	THF	10.160	11.341	3.69	1.21		10.415	119.5	4.40	2.07	1.42
	DMF	10.122	11.348	4.47	1.39	0.79	10.304	121.5	4.77	2.40	1.94
	DMSO	9.956	11.348	4.90	1.29						
	HMPA	9.661	11.348								
4-nitro-aniline (VI)	CCl_4						11.192	108.5	1.62	0.88	
	CH_3CN	10.670	11.335	4.37	1.74	0.49	10.808	119.8	4.69	2.32	1.44
	Dioxane *	10.462	11.275	4.32	1.29	0.62	10.624	120.3	4.69	2.33	1.47
	THF	10.329	11.320	4.36	1.34	0.89	10.542	120.8	4.90	2.48	1.46
	DMF	10.313	11.312	5.05	1.25	1.00	10.449	127.3	5.80	3.41	1.54
	DMSO	10.140	11.300	5.72	1.27	0.93					

(continued)

TABLE 4. Continued

	HMPA	9.757	11.270	6.18		0.63					
2,6-di-chloro--4-nitro-aniline (VII)	CCl_4						11.214	111.5	2.05	0.67	
	CH_3CN	10.612	11.268	4.20	1.74	0.95	10.786	120.3	4.79	2.44	1.00
	DMSO	10.420	11.260	4.50	1.44	1.09	10.544	120.4	4.79	2.48	1.56
	HMPA	10.210	11.229	4.76	1.51	1.30	10.357	120.5	5.01	2.59	1.56
		10.178	11.225	5.06	1.56	1.30	10.284	124.8	5.72	3.33	1.45
		10.021	11.200	5.04	1.36						
		9.634	11.200								
4-nitro-tetra-fluoroaniline (VII)	CCl_4						11.222	109.5	2.15	0.73	
	CH_3CN	10.460	11.314	4.43	2.05	0.86	10.621	121.0	5.59	2.79	1.09
	Dioxane	10.155	11.293	5.05	1.86	1.08	10.342	123.5	6.35	3.31	1.33
	THF	9.999	11.280	5.24	1.95	1.07					
	DMF	9.883	11.273	5.79	1.81	1.22					
	DMSO	9.720	11.263	6.18	1.05						
	HMPA	9.274	11.267								
4-amino-tetrafluoro-pyridine (IX)	CCl_4						11.254	109.5	2.13	0.63	
	CH_3CN	10.516	11.330	4.30	2.08	0.66	10.681	120.0	4.88	2.24	1.31
	Dioxane *	10.177	11.295	4.63	1.58		10.381	123.5	5.43	2.65	1.40
	THF	10.042	11.295	5.43	1.86	0.97					
	DMF	9.946	11.300	5.67	1.61						
	DMSO	9.765	11.282	5.66	1.50						
	HMPA	9.307	11.290								

* calculations was provided from spectral moments

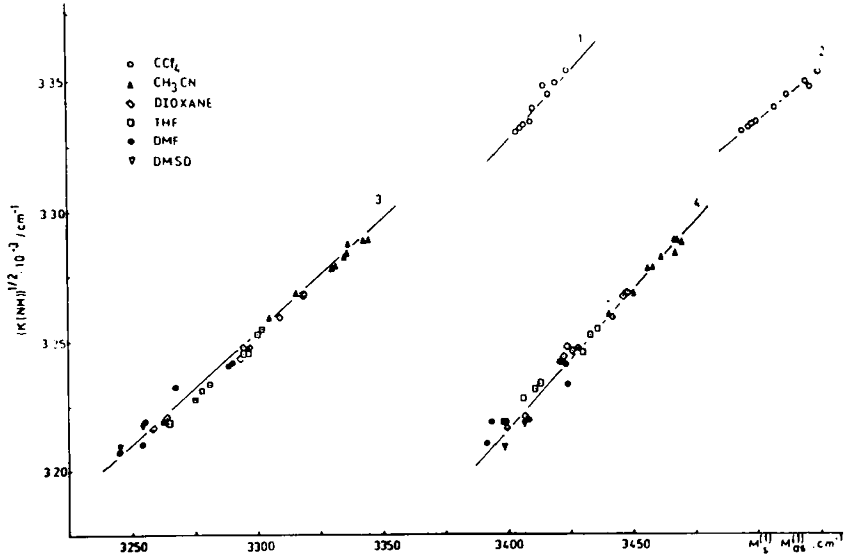

FIG. 7. The dependence of the spectral moments $M_s^{(1)}$ and $M_{as}^{(1)}$ of free (1, 2) and bound with different proton acceptors in 1:2 complexes H-bonded (3,4) molecules of I-IX compounds on the $(K(NH))^{1/2}$ value.

$$M^{(1)}_{as,m} = 1.295(KNH))^{1/2} - 829.8 \qquad r=0.996 \qquad (3)$$

For 1:2 complexes, Fig.8 (3,4), they will look like:

$$M^{(1)}_{s,c} = 1.152(K(NH))^{1/2} - 477.5 \qquad r=0.992 \qquad (4)$$

$$M^{(1)}_{as,c} = 0.925(K(NH))^{1/2} + 425.9 \qquad r=0.990 \qquad (5)$$

Analogous (4,5) linear correlations were observed and for monosubstituted anilines [2]. In this case parameters a in linear regression equations have practically the same values whereas parameters b differ by several tens cm^{-1}.

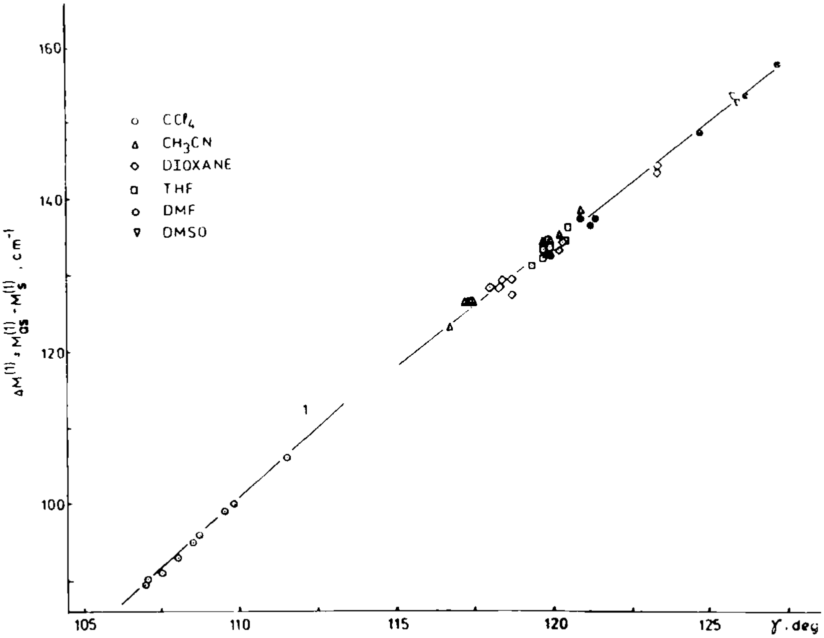

FIG. 8. The correlation between $\Delta M^{(1)}=M_{as}^{(1)}-M_{s}^{(1)}$ of free and bound H-bonded (1:2) molecules of substituted anilines I-IX with the value of valent angle γ(HNH).

The first spectral moments difference $\Delta M^{(1)}=M_{as}^{(1)}-M_{s}^{(1)}$ for free and H-bonded (1:2) molecules is in good agreement with valent angle γ(HNH) value, Fig.8.

For monomers it will be:

$$\Delta M_{m}^{(1)} = 3.729\gamma(HNH)) + 309.6 \quad r=0.999 \qquad (6)$$

and for 1:2 complexes:

$$\Delta M_{c}^{(1)} = 3.143\gamma(HNH)) + 243.9 \quad r=0.994 \qquad (7)$$

In the case of aniline and mono-(methyl, fluoro, chloro, bromo)-substituted anilines [2] the next general regularity for free and H-bonded molecules was observed:

$$\Delta M_{m,c} = 3.425\gamma(HNH)) + 278.0 \qquad r=0.995 \qquad (8)$$

Hence, with increase of combined inductive influence of substituents in aniline arene ring on amino group state the type of dependence of spectral difference $\Delta M^{(1)}=M_{as}^{(1)}-M_{s}^{(1)}$ for monomers and H-bonded 1:2 complexes on valent angle γ(HNH) value changes.

Force constants of bonded NH-groups in H-bonded 1:1 and 1:2 complexes of I-IX with various proton acceptors aren't equivalent, Table 4. The relationship between force constants K(NH) for complexes of various composition is illustrated in Fig.9. Shown dependence can be approximated by linear regression with sufficiently high correlation coefficient **r**.

$$K(NH)(1{:}1) = 0.990K(NH)(1{:}2) - 0.0746\cdot 10^{6} \qquad r=0.962 \qquad (9)$$

that is straight line practically parallel to bisectrix of coordinate angle, Fig.9. In the case of weaker proton acceptors this dependence is apparently not linear [2]. The analysis of correlation (9) indicates that the transfer from H-bonded 1:1 complexes to 1:2 complexes is accompanied by the increase of dynamic constant K(NH) of bonded groups that means deterioration of intermolecular H-bond. As this takes place, the increment in the constant K(NH) is little affected by complex type and has a value $\Delta K(NH) \cong 0.075\cdot 10^{6} cm^{-2}$.

Energy non-equivalence of H-bonds in 1:1 and 1:2 complexes of fluoroaromatic amines V, VIII, IX with THF and HMPA was studied in [8,9].The enthalpy of H-bond in 1:1 complexes of indicated substances with THF was found to exceed corresponding value for 1:2 complexes by 18-44%. For complexes

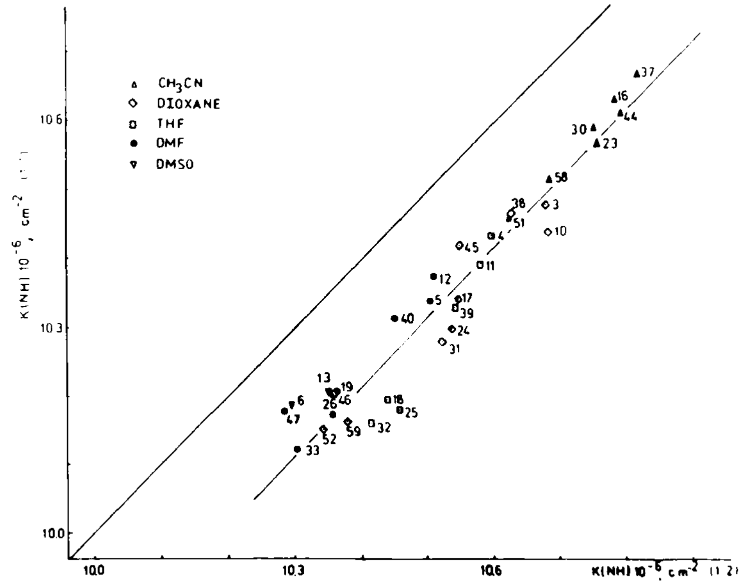

FIG. 9. The correlation between force constants of NH-bonds in H-bonded 1:1, 1:2 complexes of I-IX compounds with different proton acceptors.

containing HMPA this difference ranges from 66 to 94% i.e. with increase of H-bond power energy non-equivalence also rises.

According to empirical Iogansen equation [10,11] an energy of H-bonded complexesis proportional to an increment of dipole moment derivative with respect to normal coordinate in moving from free molecules to associated ones:

$$-\Delta H = \beta \cdot \Delta\partial\mu / \partial Q \qquad (10)$$

To test the validity of equation (10) for NH-donors we have checked more than 40 corresponding compounds and their H-bonded complexes. It was found that similar dependence really exhists, however, it isn't of general purpose character as it was supposed in [10,11]. The coefficient of proportionality β in equation (10) depends on NH-donor type. By assuming that β doesn't depend on complex composition [11], it's possible to find a correlation between energies of 1:1 and 1:2 complexes (rated per one bond) on a basis of measuring integral intensities of absorption bands of symmetrical amino group vibrations in complexes of various composition:

$$\frac{\Delta H_1}{\Delta H_2} = \frac{2\Delta(\partial\mu / \partial Q_s)(1{:}1)}{\Delta(\partial\mu / \partial Q_s)(1{:}2)} = \frac{2[(B_c^*)^{1/2}(1{:}1) - (B_m^*)^{1/2}]}{(B_c^*)^{1/2}(1{:}2) - (B_c^*)^{1/2}} \qquad (11)$$

where

$$B_c^* = \frac{9n}{(n^2+2)^2} \cdot B_c \qquad (12)$$

n -refraction coefficient of the medium.

The values of $\Delta H_1/\Delta H_2$ for complexes of I-IX with proton acceptors calculated with the formula (11) are given in Table 4.

Unfortunately, in veiw of overlapping absorption bands in the region of amino group stretching vibrations there was no opportunity to determine integral intensities of amino group absorption bands for all 1:2 complexes under study and so to calculate $\Delta H_1/\Delta H_2$ by formula (11). For this reason it was impossible to compare rated values $\Delta H_1/\Delta H_2$ for complexes of V, VIII, IX with THF and HMPA with corresponding data of works [8,9]. However, experimental correlations $\Delta H_1/\Delta H_2$ for complexes of mentioned compounds with THF can be compared with rated for complexes with dioxane, Table 4, which is most close solvent to THF in proton accepting features. Found differences are not more than 10-15%. Taking into account instrumental error in measuring integral intensities the agreement between these two values can be considered to be wholly satisfactory.

For the weakest proton donors I and II calculation for a sequence of proton acceptors: acetonitrile, THF, DMF, DMSO give in the beginning some fall of correlations $\Delta H_1/\Delta H_2$ from 1.2 (CH_3CN) to 0.95 (DMF) and then their increase in complexes with DMSO to 1.07 (I) and 1.40 (II). So our further interest is to check this regularity basing on experimental measurements of energies for H-bonded complexes of I, II with various proton acceptors. In the other cases (compounds III-IX) with increase of proton accepting power energy non-equivalence of NH-bonds in 1:1 and 1:2 complexes grows, this fact being in agreement with deductions made in [8,9].

Thus, it's possible to say that formula (11) reflects adequately the tendency in changes of energy non-equivalence of NH-bonds in 1:1 and 1:2 complexes depending on proton acceptor power.

Electrooptical non-equivalence of amino group NH-bonds in various complexes of I-IX is presented in Fig.10. All points in this figure are placed below "equivalence straight line" that is indicative of the enhancement of electrooptical parameters $\partial\mu/\partial q$of H-bonded NH-groups in 1:2 complexes in comparison with analogous parameters $\partial\mu/\partial q_1$ of 1:1 complexes. In the majority of cases this enhancement lays in the range 25-30%, Table 4.

The values of $\partial\mu/\partial q'$ parameters for 1:2 complexes far exceed $\partial\mu_i/\partial q_j$ parameters (i, j =1, 2; i≠j). Thus, the change-over from 1:1 complexes to 1:2 ones is accompanied by the increase of electrooptical interaction of amino group NH-bonds.

Based on comparative analysis of Badger-Bauer [12] and Ioganssen [11] equations definite dependence between electrooptical parameters $\partial\mu/\partial q$, $\partial\mu/\partial q'$ and $(K(NH))^{1/2}$ values should be expected . Fig. 11 depicts this dependence for free molecules (1, 1') and H-bonded 1:2 complexes (2, 2', 3, 3'). It can be seen that, to a first approximation, these dependences are practically linear both for free and H-bonded molecules.

For free molecules equations of linear regression will look like:

$$\partial\mu/\partial q = 0.0296(K(NH))^{1/2} - 97.3 \quad r=0.869 \qquad (13)$$

$$\partial\mu/\partial q' = 0.0190(K(NH))^{1/2} - 62.8 \quad r=0.799 \qquad (14)$$

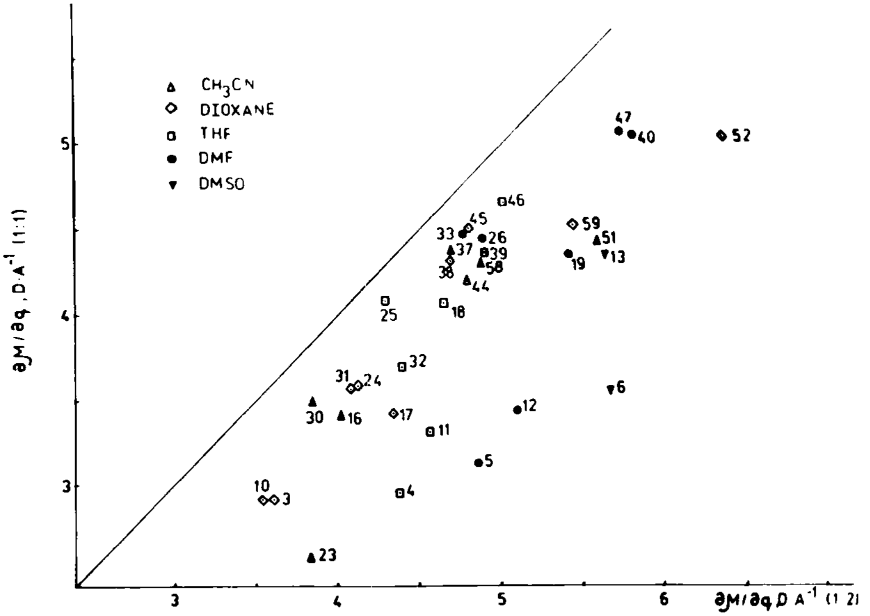

FIG. 10. The correlation of the values of electrooptical parameters ∂μ/∂q of bound NH-group I-IX compounds in H-bonded 1:1, 1:2 complexes.

Among 1:2 complexes of I-IX with different proton acceptors the complexes with acetonitrile (Fig. 11; 2, 2') stand out, for which:

$$\partial\mu / \partial q = -0.0561(K(NH))^{1/2} + 188.2 \quad r=0.744 \qquad (15)$$

$$\partial\mu / \partial q' = 0.0312(K(NH))^{1/2} + 104.4 \quad r=0.641 \qquad (16)$$

In all remaining complexes containing THF, dioxane, DMF, DMSO, HMPA individual properties of proton acceptors aren't discernible practically and electrooptical parameters ∂μ/∂q and ∂μ/∂q' of 1:2 complexes obey the general regularity (Fig. 11; 3,3'):

$$\partial\mu / \partial q = -0.0280(K(NH))^{1/2} + 95.7 \quad r=0.743 \qquad (17)$$

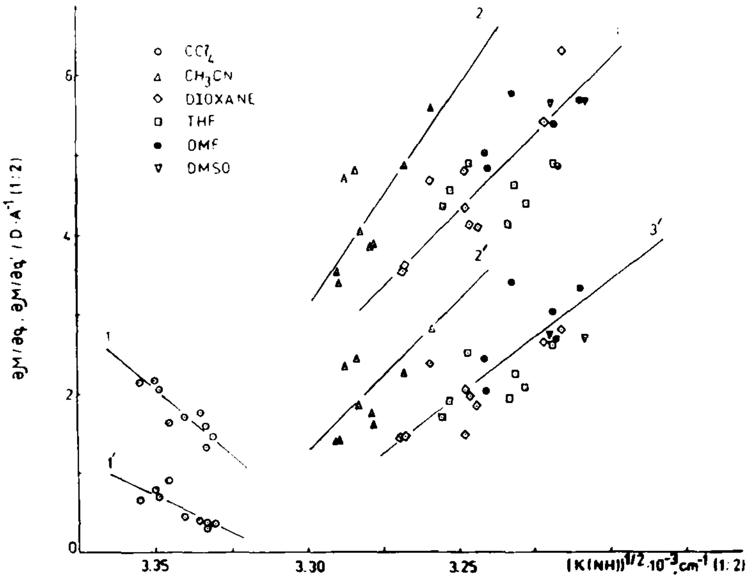

FIG. 11. The correlation between the parameters ∂μ/∂q, ∂μ/∂q' and $(K(NH))^{1/2}$ of free (1, 1') and bound with CH_3CN (2, 2') and other proton acceptors (3, 3') H-bonded molecules of I-IX compounds.

$$\partial\mu/\partial q' = -0.0221(K(NH))^{1/2} + 73.9 \quad r=0.745 \qquad (18)$$

In weaker H-bonded complexes of aniline and mono-(methyl, fluoro, chloro, bromo)-substituted anilines individual influence of proton acceptors on electrooptical parameters of amino group has been found to be much more pronounced [1].

Similar difference in changes of electrooptical parameters depending on H-bond strength can be attributed to the fact that in weak complexes the growth of the derivative ∂μ/∂q as compared with free molecules is primarily accounted for polarization of free electron pair belonging to proton acceptor. As H-bond strengthens the role of amimogroup polarization by proton acceptor becomes greater and relative contribution of this constituent to ∂μ/∂q increment increases.

Indirect verification of this hypothesis can be derived from the analysis of changes in electrooptical parameters $\partial\mu_2/\partial q_2$ of free NH-group in 1:1 complexes, Table 4. For I-IX relative decreases in values of parameter $\partial\mu_2/\partial q_2$ with H-bond enhancement are considerably more than those for aniline and mono-(methyl, fluoro, chloro, bromo)-substituted derivatives [1].

Hence, proton donating properties of substituted anilines in intermolecular H-bonded complexes along with spectral, geometrical, dynamic, electrooptical and energy characteristics of amino group NH-bonds were found to depend essentially on the position, the number and the type of substituents.

The correlation of these parameters in H-bonded 1:1 and 1:2 complexes with different proton acceptors is also determined by the position, number and properties of substituents in aniline arene ring.

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