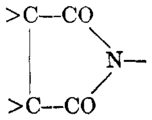
solution. The amine hydrochloride was precipitated. The crystals were collected and washed with ether. Intermediate II hydrochloride was obtained: yield, 88 mg; mp 223–224°; $[\alpha]^{25}\text{D}$ −47.5° (*c* 0.75, absolute ethanol). Infrared absorption bands at 1785 and 1710 cm^{-1} showed that the compound has a N-substituted succinimide structure, below. A band at 1745 cm^{-1} disappeared after the purification procedure.



Anal. Calcd for $C_{20}H_{23}N_2O_2Cl$: C, 66.93; H, 6.46; N, 7.81. Found: C, 66.71; H, 6.58; N, 7.79.

Intermediate II hydrochloride was liberated with aqueous sodium hydrogen carbonate. The free amine was extracted with ether. The solution was dried and the solvent was evaporated. Infrared absorption bands of the free intermediate II were recorded. The compound showed the same characteristic bands of N-substituted succinimide at 1780 and 1710 cm^{-1}. Intermediate II did not crystallize.

The crude oil, 0.8 g, was hydrolyzed with 6 *N* hydrochloric acid, 15 ml, in the same way as above. The resulting aspartic acid was treated with 1-fluoro-2,4-dinitrobenzene. DNP-aspartic acid was separated by column chromatography. DNP-(*S*)-aspartic acid was obtained: $[\alpha]^{25}\text{D}$ +14.2° (*c* 0.18 1 *N* NaOH).

Reaction c. (*S*)-Aspartic acid from Diethyl fumarate and (*S*)-amine.—A mixture of ethyl fumarate, 1.72 g, and (*S*)-amine, 4.3 g, was heated at 115-120° for 3 days. The reaction mixture was hydrolyzed and then hydrogenolyzed in a similar way as described above. (*S*)-Aspartic acid, 1.15 g (87%), was obtained: $[\alpha]^{25}\text{D}$ +2.0° (*c* 3.90, 5 *N* HCl).

Anal. Found: C, 35.89; H, 5.47; N, 10.31.

DNP-(*S*)-aspartic acid had $[\alpha]^{25}\text{D}$ +4.3° (*c* 1.08, 1 *N* NaOH), mp 195–197° dec.

(*R*)-Aspartic acid was prepared as above from diethyl fumarate, 1.7 g, and (*R*)-amine, 4.3 g: yield, 1.11 g (85%); $[\alpha]^{25}\text{D}$ −1.6° (*c* 3.98, 5 *N* HCl).

DNP-(*R*)-aspartic acid had $[\alpha]^{25}\text{D}$ −4.2° (*c* 1.03, 1 *N* NaOH), mp 191–193° dec.

(±)-Aspartic acid was prepared by the use of (±)-amine under the same reaction conditions: yield, 1.13 g (86%).

Anal. Found: N, 10.28.

Isolation of Intermediates in Reaction c.—Isolation of intermediates in reaction c was carried out in a similar way as described in reaction b. The crude crystals, 0.92 g, were obtained. The crystals were recrystallized from ethanol. Pure intermediate I, 0.70 g, was obtained: mp 121–123°; $[\alpha]^{25}\text{D}$ −112.0° (*c* 0.87, absolute ethanol); infrared absorption bands, 1645 (amide I), 1555 cm^{-1} (amide II).

Anal. Found: C, 75.65; H, 7.59; N, 9.45.

A part of the crude intermediate II was hydrolyzed and then hydrogenolyzed in a similar way as described above. The resulting aspartic acid was dinitrophenylated and the DNP-aspartic acid was separated by column chromatography. The sample amounts were too small to accurately measure optical rotation.

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Application of the Hammett Equation to Substituent Effects on π Donors in Charge-Transfer Complex Formation. I. Singly Substituted Donors

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The effect of substituents in π donors on charge-transfer complex formation equilibrium was studied by correlation of the equilibrium constants with the extended form of the Hammett equation. Twelve sets of substituted benzene donors (two of which have constant substituents on the ring), four sets of substituted naphthalene donors, and one set of 1-substituted propene donors were studied. The results of the correlations are generally very good. The composition of the electrical effect appears to depend on donor type but seems to be independent of the acceptor with the exception of silver(I) ion complexes. For the benzene sets the average value of ε is about 1.3 [excluding the silver(I) ion complexes for which ε is 0.37]. The magnitude of the electrical effect is a function of acceptor strength. Electrical effects on complex formation are much smaller than on such reactions as electrophilic aromatic substitution and deuterium exchange in liquid ammonia. Steric effects are observed in some complexes.

We have for some time been interested in the application of the Hammett equation[1] to the effect of sub-

$$Q_X = \rho\sigma_X + Q_H \qquad (1)$$

stituents in nonaromatic unsaturated systems.[2] It seemed of interest to extend these studies to substituent effects on charge-transfer complex formation[3] between substituted olefin donors and various acceptors. For comparison, we need to know the nature of substituent effects in complex formation by substituted aromatic donors. Although sporadic attempts have been made to correlate equilibrium constants for charge-transfer complex formation with the Hammett equation,[4] no comprehensive study of the available data is extant. We have, therefore, correlated equilibrium constants taken from the literature with the extended form of the Hammett equation by means of

$$Q_X = \alpha\sigma_I + \beta\sigma_R + Q_H \qquad (2)$$

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[1] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons Inc., New York, N. Y., 1956, p 565; V. A. Palm, *Russ. Chem. Rev.*, **31**, 471 (1961); R. R. Wells, *Chem. Rev.*, **63**, 171 (1963); C. D. Ritchie and W. F. Sager, Jr., *Progr. Phys. Org. Chem.*, **2**, 323 (1963).

[2] M. Charton, *J. Am. Chem. Soc.*, **80**, 5940 (1958); *J. Org. Chem.*, **26**, 735 (1961); *ibid.*, **30**, 552, 557, 969, 974 (1965).

[3] L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964.

[4] Of the previous applications of the Hammett equation to charge-transfer complex equilibria, only that of L. J. Andrews and R. M. Keefer [*J. Am. Chem. Soc.*, **72**, 3113 (1950)] is concerned with the type of system discussed in this paper, monosubstituted benzenes in which the benzene ring itself is a π donor. Papers have recently appeared in which equilibrium constants for substituted benzenes bearing an *n*- or π-donor reaction site external to the benzene ring were correlated with the Hammett equation: J. vander Veen and W. Stevens, *Rec. Trav. Chim.*, **82**, 287 (1963); T. Fueno, T. Okuyama, T. Deguchi, and J. Furukawa, *J. Am. Chem. Soc.*, **87**, 170 (1965). M. Tamres [*J. Phys. Chem.*, **68**, 2621 (1964)] has reported the correlation of multiply substituted benzene formation constants with the σ* constants.

Table I

Charge-Transfer Complex Formation Constants Used in Correlations[a]

1. Bromine-substituted benzene in CCl_4 at 25°[b]

X	H	Me	Cl	Br	I
K_N	1.04	1.44	0.90	1.18	1.59

2. Iodine monochloride substituted benzene in CCl_4 at 25°[c]

X	H	Me	Cl	Br	*t*-Bu
K_N	4.76	7.97	2.24	3.43	8.70

3. Iodine monochloride substituted benzene in CCl_4 at 25°[d]

X	H	Me	Et	*i*-Pr	*t*-Bu	Br	$PhCH_2CH_2$
K_C	0.54	0.87	0.88	0.88	0.88	0.32	0.74[e]

4. Iodine monochloride substituted toluene in CCl_4 at 25°

X	4-Me	4-Cl	3-Cl	4-MeO	3-Me	H
K_C	1.85[f]	0.32[f]	0.24[f]	5.19[f]	1.39[d]	0.87[d]

5. Iodine-substituted benzene in CCl_4 at 25°[d]

X	H	Me	Br	$PhCH_2CH_2$
K_C	0.15	0.16	0.13	0.23[d]

6. Iodine-substituted benzene in cyclohexane at 25°[g]

X	H	Me	Et	Cl	Br	Ph
K_C	0.212	0.293	0.263	0.101	0.127	0.178[e]

7. Maleic anhydride substituted benzene in $CHCl_3$ at 25°[h]

X	H	Me	OMe	NMe_2
K_N	0.68	0.60	0.84	1.5

8. Tetracyanoethylene-substituted benzene in CH_2Cl_2 at 22°[i]

X	MeO	Me	Ph	H	Br	Cl	I
K_N	4.42	3.70	2.045[d]	2.00	0.611	0.770	1.24

9. Pyromellitic anhydride substituted benzene in CCl_4 at 26°[j]

X	H	Me	Et	*i*-Pr	*t*-Bu	OMe	Cl
K_N	3.05	5.03	5.68	3.86	4.00	7.75	2.08

10. Chloranil-substituted benzene in cyclohexane at 18°[k]

X	H	Me	Et	*i*-Pr	MeNH
K_C	0.79	1.37	1.04	0.80	7.9

11. Picric acid 1-substituted naphthalene in $CHCl_3$ at 27°[l]

X	H	Me	Et	*i*-Pr	F	Cl	Br	I	MeO	EtO	*i*-PrO	Ac
K_C	2.31	3.16	2.61	1.87	1.49	1.87	2.06	2.13	4.89	5.78	4.81	2.76

12. Picric acid 2-substituted naphthalene in $CHCl_3$ at 27°[l]

X	H	Me	Et	*i*-Pr	F	Cl	Br	I	MeO	EtO	*i*-PrO	Ac
K_C	2.31	3.50	2.77	2.51	1.28	1.50	1.57	1.62	3.30	3.01	3.09	2.47

13. Picric acid 1-substituted naphthalenes in $CHCl_3$ at 28.5° by spectrophotometry[m]

X	H	Me	Et	*i*-Pr	F	Cl	Br	MeO	EtO	*i*-PrO	C_2H_3
K_C	1.13	1.47	1.41	0.97	0.55	0.43	0.51	2.78	3.76	2.87	2.13

14. Picric acid 2-substituted naphthalenes in $CHCl_3$ at 28.5° by spectrophotometry[m]

X	H	Me	Et	*i*-Pr	*t*-Bu	F	Cl	Br	MeO	EtO	*i*-PrO	C_2H_5
K_C	1.13	1.76	1.45	1.35	1.16	0.33	0.34	0.43	1.48	2.11	1.66	1.79

15. 1,3,5-Trinitrobenzene-substituted aniline in EtOH at 25°[n]

X	3-Me	$3\text{-}CO_2H$	$4\text{-}CO_2H$	4-EtO	4-Ac	H	4-Cl	4-CN	$3\text{-}CF_3$
K_C	0.740	0.69	0.605	0.458	0.44	0.397	0.35	0.22	0.17

16. Silver(I)-substituted benzene in water at 25°

X	MeO	Ac	CO_2Et	F	Cl	Br	NO_2	H	Me	
K_C	2.50	0.54	0.56	0.46	0.69	0.97	0.19	2.41	2.95	
	p	*p*	*p*	*p*	*p*	*p*	*p*	*o*	*o*	
X	Ph	$PhCH_2$	$PhCH_2CH_2$	Et	Pr	i-Pr	s-Bu	t-Bu	Bu	OH
K_C	1.97[d]	1.73[d]	4.0[d]	2.7	2.9	2.8	2.4	2.3	3.0	1.54
	o	*o*	*o*	*q*	*q*	*q*	*q*	*q*	*r*	

17. Silver(I) *trans*-3-substituted propenes in water at 25°

X	CO_2H	CHO	CH_2OH	Et	Me
K_C	0.09	0.19	5.17	62.2	29.2
	s	*s*	*s*	*t*	*u*

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[a] X = substituent, K_C = concentration equilibrium constants in liter $mole^{-1}$; K_N = equilibrium constants in mole fraction. [b] R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **72,** 4677 (1950). [c] R. M. Keefer and L. J. Andrews, *ibid.*, **72,** 5170 (1950). [d] L. J. Andrews and R. M. Keefer, *ibid.*, **74,** 4500 (1952). [e] Includes 0.5. [f] N. Ogimachi, L. J. Andrews, and R. M. Keefer, *ibid.*, **77,** 4202 (1955). [g] W. K. Plucknett and H. L. Richards, *J. Chem. Eng. Data*, **8,** 239 (1963). [h] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **75,** 3776 (1953). [i] R. E. Merrifield and W. D. Philips, *ibid.*, **80,** 2781 (1958). [j] L. L. Ferstandig, W. G. Toland, and C. D. Heaton, *ibid.*, **83,** 1151 (1961). [k] E. A. Halevi and M. Nussim, *J. Chem. Soc.*, 876, (1963). [l] P. D. Gardner and W. E. Stump, *J. Am. Chem. Soc.*, **79,** 2759 (1957). [m] P. D. Gardner, R. L. Brandon, N. J. Nix, and I. Y. Chang, *ibid.*, **81,** 3413 (1959). [n] S. D. Ross, M. Bassin and I. Kuntz, *ibid.*, **76,** 4176 (1954). [o] L. J. Andrews and R. M. Keefer, *ibid.*, **71,** 3644 (1949). [p] Reference 4, L. J. Andrews and R. M. Keefer. [q] L. J. Andrews and R. M. Keefer, *ibid.*, **72,** 5034 (1950). [r] R. M. Keefer, L. J. Andrews, and R. E. Kepner, *ibid.*, **71,** 3906 (1949). [s] S. Winstein and H. J. Lucas, *ibid.*, **60,** 836 (1938). [t] H. J. Lucas, R. S. Moore, and D. Pressman, *ibid.*, **65,** 227 (1943). [u] F. R. Hepner, K. N. Trueblood, and H. J. Lucas, *ibid.*, **74,** 1333 (1952).

TABLE II

SUBSTITUENT CONSTANTS[a]

X	σ_I	Reference	σ_p	Reference	X	σ_I	Reference
$PhCH_2CH_2$	...	...	−0.14	*b*	NHMe	0.10	*c*
C_2H_3	...	...	−0.02	*d*	NMe_2	0.10	*b*
CH_2OH	...	...	−0.01	*e*	NO_2	0.68	*f*
CHO	0.36	*g*	0.42	*g*			

[a] Taken from sources other than ref 5 and 6. [b] M. Charton, *J. Org. Chem.*, **30**, 969 (1965). [c] Assumed equal to σ_I for NMe_2 and NH_2. [d] Estimated from $\sigma_{p,XCH=CH} = \sigma_{p,X} + q$. M. Charton, Ph.D. Dissertation, Stevens Institute of Technology, Hoboken, N. J., 1962. [e] O. Exner and J. Jonas, *Collection Czech. Chem. Commun.*, 29, 2296 (1962). [f] We have reported a value of σ_I (ref 5) for this group of 0.76 which seems much too high when compared with $\sigma_{m,NO_2} = 0.710$. R. W. Taft Jr., and I. C. Lewis [*J. Am. Chem. Soc.*, **81**, 161 (1959)] give a value of 0.63 based on aliphatic reactivities which seems too low. We have, therefore, used the value of Taft and Lewis based on aromatic reactivities. [g] Footnote *b*, p 552.

TABLE III

RESULTS OF CORRELATIONS WITH EQUATION 2

Set	$-\alpha$	$-\beta$	Q_H	R[a]	F[b]	S_{est}[c]	$S\alpha$[c]	$S\beta$[c]	r[d]	cl[e]	n[f]
1	0.0259	−0.175	0.112	0.221	0.0513	0.139	0.434	1.16	0.778	90	5
1A	0.470	0.883	0.0246	0.802	0.904	0.0895	0.360	0.918	0.859	90	4
2	1.17	1.27	0.688	0.964	12.96	0.0939	0.279	0.803	0.791	90	5
3	1.1	1.16	−0.259	0.988	84.81	0.0310	0.0893	0.256	0.641	99.5	7
4A	2.11	2.56	−0.101	0.997	97.03	0.0635	0.183	0.198	0.556	90	4
5	0.475	0.728	−0.825	0.754	0.658	0.120	0.422	1.10	0.717	90	4
6	0.909	0.647	−0.684	0.976	30.73	0.180	0.174	4.83	0.848	97.5	6
7	0.231	0.439	−0.227	0.958	5.530	0.0879	0.476	0.149	0.593	90	4
8	1.52	1.25	0.339	0.948	17.75	0.127	0.262	0.342	0.408	97.5	7
8A	1.7	1.51	0.305	0.995	153.3	0.0444	0.103	0.129	0.505	99.5	6
9	0.934	1.22	0.475	0.933	13.38	0.0823	0.207	0.255	0.617	97.5	7
10	0.0142	1.49	−0.136	0.979	22.73	0.121	2.03	0.460	0.878	95.0	5
11	0.363	0.477	0.409	0.594	2.455	0.167	0.254	0.228	0.357	90	12
11A	0.576	0.874	0.328	0.797	6.949	0.133	0.220	0.242	0.504	97.5	11
11B	0.684	0.850	0.380	0.848	8.992	0.120	0.208	0.219	0.458	97.5	10
12	0.594	0.236	0.443	0.792	7.592	0.101	0.153	0.138	0.357	97.5	12
12A	0.747	0.524	0.384	0.928	24.70	0.0654	0.108	0.119	0.504	99.5	11
13	1.49	1.58	−0.0139	0.878	13.50	0.173	0.317	0.342	0.614	99.5	11
13A	1.49	1.71	−0.0835	0.932	23.17	0.137	0.250	0.276	0.600	99.5	10
13B	1.59	1.68	−0.0297	0.954	30.28	0.121	0.231	0.246	0.557	99.5	9
14	1.52	1.04	0.0258	0.895	18.09	0.144	0.252	0.285	0.635	99.5	12
14A	1.53	1.15	−0.0237	0.933	26.73	0.120	0.210	0.242	0.628	99.5	11
14B	1.63	1.15	0.0145	0.954	35.53	0.106	0.194	0.214	0.600	99.5	10
15A	0.357	0.352	−0.405	0.985	16.67	0.0408	0.0927	0.0889	0.0837	90.0	4
16	1.45	0.533	0.334	0.961	95.49	0.107	0.107	0.123	0.111	99.5	19
16A	1.44	0.64	0.327	0.965	101.6	0.104	0.104	0.144	0.0731	99.5	18
16B	1.32	0.435	0.354	0.916	31.48	0.113	0.206	0.312	0.720	99.5	15
17	3.60	5.21	0.794	0.987	38.93	0.286	3.18	6.41	0.976	95	5

[a] Multiple correlation coefficient. [b] F test for significance of regression. [c] Standard errors of estimate, α and β, respectively. [d] Partial correlation coefficient of σ_I on σ_R. [e] Confidence level. [f] Number of points in the set.

least-mean-square multiple linear regression analysis. Our choice of eq 2 is determined by the lack of an *a priori* method of determining what substituent constant would be appropriate for use with eq 1. The data used in the correlations are set forth in Table I. The σ_I constants required were taken from our compilation[5] when possible. The σ_R constants were obtained from

$$\sigma_R = \sigma_p - \sigma_I \qquad (3)$$

The necessary σ_p constants were taken from the collection of McDaniel and Brown[6] when possible. In some cases it was necessary to correlate data with eq 1 by means of the σ_I, σ_m, σ_p°, σ_p, and σ_p^+ constants. The σ_m constants were taken from McDaniel and Brown,[6] and the σ_p° from Ritchie and Sager,[1] and the σ_p^+ constants from Brown and Stock.[7] Substituent constants from sources other than those cited above are given in Table II.

Some of the substituted benzene sets studied include compounds having two benzene rings, such as diphenyl, diphenylmethane, or 1,2-diphenylethane. For these compounds a statistical factor of 0.5 has been applied to their equilibrium constants as these compounds have two potential donor sites.

Results

The results of the correlations with eq 2 are presented in Table III and the results of correlations with eq 1 are presented in Table IV.

For purposes of further discussion we shall classify the sets studied as follows: I, substituted benzene π donors–halogen acceptors; II, substituted benzene π donors–π acceptors; III, substituted naphthalene π donors–π acceptors; IV, substituted aniline donor–*sym*-trinitrobenzene acceptor; V, substituted benzene π donor–silver(I) ion acceptor; and VI, *trans*-1-substituted propene π donor–silver(I) ion acceptor.

Class I.—No correlation is obtained with set 1. Elimination of iodobenzene from the set leads to results

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(5) M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).

(6) D. H. McDaniel and H. C. Brown, *ibid.*, **23**, 420 (1958).

(7) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

TABLE IV

RESULTS OF CORRELATION WITH EQUATION 1

Set	$-\rho$	Q_H	r^a	s^b	$s_\rho{}^c$	t^d	n^e	cl^f
1B I	0.289	0.0837	0.793	0.0901	0.222	1.302	3	50
m	0.364	0.801	0.827	0.0831	0.247	1.472		60
p°	0.456	0.0614	0.928	0.0551	0.183	2.489		70
p	0.501	0.0527	0.955	0.0439	0.156	3.218		80
p$^+$	0.475	0.0120	0.9991	0.00624	0.0204	23.30		95
4	2.00	0.0227	0.977	0.118	0.217	9.214	6	99
4B I	1.36	0.0108	0.985	0.0963	0.237	5.713	3	80
m	1.65	−0.0119	0.993	0.0641	0.190	8.663		90
p°	1.85	−0.105	0.995	0.0555	0.185	10.01		90
p	1.95	−0.142	0.984	0.100	0.356	5.484		80
p$^+$	1.55	−0.281	0.866	0.280	0.899	1.728		60
15B I	1.17	−0.289	0.943	0.151	0.412	2.842	3	70
m	1.13	−0.298	0.953	0.137	0.359	3.150		80
p°	0.875	−0.323	0.975	0.101	0.199	4.393		80
p	0.847	−0.329	0.979	0.0919	0.175	4.834		80
p$^+$	0.680	−0.366	0.995	0.0443	0.0667	10.19		90

[a] Correlation coefficient. [b] Standard deviation of the estimate. [c] Standard deviation. [d] "Student" t test. [e] Number of points in the set. [f] Confidence level.

which, although greatly improved, are still not significant (1A). Andrews and Keefer have suggested that iodobenzene and possibly also bromobenzene may behave as *n* rather than π donors. If this is indeed the case, these two compounds are not members of this set. Although the three remaining compounds in the set are not sufficient to provide a certain test of meaningful correlation with the Hammett equation, we felt that they were worth examining. Equation 2 cannot be used for this purpose as at least four points are required for multiple linear regression analysis. We have, therefore, correlated the remaining points of set 3 with eq 1 by means of the σ_I, σ_m, $\sigma_p{}^\circ$, σ_p, and $\sigma_p{}^+$ constants (set 1B). The results support the contention that these compounds are different in their behavior from bromobenzene and iodobenzene, the $\sigma_p{}^+$ constants giving the best correlation.

Sets 2 and 3 both give good correlation with eq 2. Set 4 has been divided into two subsets, 4A and B. Set 4A includes the 4-XC_6H_4Me, X = H, Cl, MeO, and Me; set 4B includes the 3-XC_6H_4Me, X = H, Me, and Cl. The results for set 4A correlated with eq 2 are excellent. Correlation of 4B with eq 1 shows best results with σ_m and $\sigma_p{}^\circ$; the correlation is not highly significant.

Set 5 does not give meaningful results. With set 6, very good results are obtained. As there is significant correlation between σ_I and σ_R for this set, the values of α and β are not reliable.

Class II.—Significant correlation is not obtained with set 7. Set 8 gives good results, which are improved by excluding iodobenzene from the set (8A). Here, as in set 1, the iodobenzene may be functioning as an n donor. Sets 9 and 10 also give good results, although for set 10 the high degree of correlation between σ_I and σ_R makes the values of α and β unreliable.

Class III.—Results obtained for set 11 are not significant. Elimination of the value for X = acetyl gives very much improved correlation (11A). Further exclusion of the isopropyl value gives somewhat improved results (11B). Set 12 gives good results, on elimination of the acetyl value, the correlation is excellent (12A). An excellent correlation is obtained with set 13, which is improved on the exclusion of the value for X = vinyl (13A) and further improved with the additional exclusion of the value for X = isopropyl (13B). Excellent results are also shown by set 14. Elimination of the value for X = vinyl improves the correlation 14A, further improvement is effected by also omitting the value for X = *t*-Bu. The deviation of the values for X = vinyl in sets 13 and 14 is probably due to complex formation between picric acid and the vinyl group. The magnitude of the observed formation constant is in accord with this explanation. A possible reason for the deviation of the acetyl group in sets 11 and 12 is hydrogen bond formation between the carbonyl oxygen and the picric acid. The deviations of the isopropyl group in sets 11 and 13, and the tertiary butyl group in set 14 will be discussed below.

Class IV.—We have chosen to consider set 15 separately because of the uncertainty as to whether the nitrogen atom is acting as an n donor or the aromatic ring as a π donor. Only the *para*-substituted compounds have been included in the subset 15A. We have excluded the values of X = CO_2H and X = Ac since they obviously deviate considerably. We consider the deviation of the former to be due to the formation of a hydrogen-bonded complex between the CO_2H and NH_2 groups, the latter possibly to complex formation between the carbonyl carbon and the amino group. The remainder of the set gives good results. We have examined the correlation of the 3-$XC_6H_4NH_2$ (X = Me, CF_3, H) with eq 1. Best results are obtained with $\sigma_p{}^+$. The correlation is not highly significant.

Class V.—Set 16 gives excellent correlation. In order to determine whether phenol was acting as a π donor or an n donor it was excluded from the set. Correlation of the remaining data of 16A gave results not significantly different from 16. We have also examined the effect of further omitting all of the substituents that are electron acceptors by resonance (X = nitro, acetyl, carbethoxy, set 16B). The results obtained are not so good although still significant at the 99.5% confidence level.

Class VI.—Good results are obtained for this set. The high degree of correlation between σ_I and σ_R for this set makes the values obtained for α and β very unreliable.

Our results show that in general, substituent effects on equilibrium constants for charge-transfer complex formation are successfully represented by eq 2. It should be noted, however, that of the sets studied, only 15–17 include substituents which are electron donors by resonance. We may now consider the problem of the nature and magnitude of the electrical effect and the presence of steric effects.

Discussion

Composition of the Electrical Effect.—The composition of the electrical effect may be conveniently described by the equation[8]

$$\epsilon = \beta/\alpha \qquad (4)$$

where α and β are defined by eq 2. Values of ϵ for the sets studied are reported in Table V. For those sets correlated with eq 1, ϵ has been taken to be that of the substituent with which best correlation was obtained. If correlation is equally good with two substituent constants, an average of their ϵ values is given in Table V. The values of ϵ for the substituent constants used with eq 1 are σ_I, 0; σ_m, 0.33; $\sigma_p{}^\circ$, 0.67; σ_p, 1.0; $\sigma_p{}^+$, 1.60.

TABLE V

VALUES OF ϵ FOR SETS STUDIED

Set	Donor	Acceptor[b]	Solvent	ϵ
1B	PhX	Br_2	CCl_4	1.6
2	PhX	ICl	CCl_4	1.09
3	PhX	ICl	CCl_4	1.05
4A	4-MeC_6H_4X	ICl	CCl_4	1.21
4B	3-MeC_6H_4X	ICl	CCl_4	0.5
5	PhX	I_2	CCl_4	1.53
6	PhX	I_2	Cyclohexane	0.71
7	PhX	MA	$CHCl_3$	1.90
8B	PhX	TCNE	CH_2Cl_2	0.853
9	PhX	PMA	CCl_4	1.31
10	PhX	CA	Cyclohexane	. . .[a]
11B	1-$C_{10}H_7X$	PA	$CHCl_3$	1.25
12A	2-$C_{10}H_7X$	PA	$CHCl_3$	0.701
13B	1-$C_{10}H_7X$	PA	$CHCl_3$	1.06
14B	2-$C_{10}H_7X$	PA	$CHCl_3$	0.707
15A	4-$XC_6H_4NH_2$	TNB	EtOH	0.986
15B	3-$XC_6H_4NH_2$	TNB	EtOH	1.6
16	PhX	Ag^+	H_2O	0.368
16A	PhX	Ag^+	H_2O	0.444
16B	PhX	Ag^+	H_2O	0.330
17	*trans*-MeCH=CHX	Ag^+	H_2O	1.45

[a] No value of ϵ has been calculated for this set. [b] Abbreviations used: MA, maleic anhydride; TCNE, tetracyanoethylene; PMA, pyromellitic dianhydride; CA, chloranil; PA, picric acid; TNB, *sym*-trinitrobenzene.

The average value of ϵ obtained for substituted benzene donors with halogen acceptors (sets 1B, 2, 3, 5, and 6) is 1.2; with π acceptors (sets 7–9) an average value of 1.4 is found. The difference between these values is probably not significant. With silver(I) as the acceptor, a value of ϵ of about 0.37 is obtained. It was previously proposed that substituent effects in this set were predominantly or completely inductive.[4] Our results show the presence of a significant resonance effect. We must account for the difference in behavior between silver(I) ion on the one hand and halogen or π acceptors on the other. The resonance effect is not nearly as important in the former case as in the latter. It is interesting to note that in both the halogen and the π-acceptor complexes the acceptor is usually symmetric with respect to the axis through the center of the donor ring.[3] In these complexes all of the carbon atoms in the donor ring are involved in bonding with the acceptor to the same extent. This is not true of the complexes with silver(I) ion in which the silver is above one edge of the ring, somewhat closer to one carbon than to the other. It would appear that the fundamental difference in the nature of the bonding between the two types of complex is reflected in the composition of the electrical effect of substituents. Our results suggest that for "centrosymmetric" complexes a value of ϵ of 1.3 ± 0.5 may generally be expected.

The results obtained for the two sets in which substituted naphthalenes were donors seem to show a dependence of ϵ on donor structure, the 1-substituted naphthalene giving a value of ϵ of about 1.2, whereas the 2-substituted naphthalenes give a value of ϵ of *ca.* 0.7.

The Magnitude of Substituent Effects on Complex Formation.—The magnitude of substituent effects is measured by the magnitude of ρ in eq 1 or of α in eq 2. The magnitude of α must depend on the type of donor, the acceptor, the solvent and the temperature. With respect to the dependence of α on donor structure, the value of α obtained for complex formation between silver(I) ion and *trans*-1-substituted propenes (set 17) is about twice as large as that for complex formation between silver(I) ion and substituted benzenes (set 16). No conclusion can be drawn concerning the naphthalene sets relative to the substituted benzene sets, as data for the same acceptor under the same conditions of temperature and solvent are not available.

In considering the effect of acceptor strength we may use the equation[9]

$$\log K_A = \upsilon\eta_A + \log K_A{}^\circ \qquad (5)$$

where η is a measure of acceptor strength, K_A the formation constant for some acceptor with a given donor, υ is a function of the donor, solvent, and temperature, and $\log K_A{}^\circ$ is the intercept. According to Miller,[10] variation in both donor and acceptor can now be expressed by

$$\log K_{XA} = \rho_A{}^\circ\sigma_X + \upsilon_H\eta_A + p\sigma_X\eta_A + \log K_{H,A}{}^\circ \qquad (6)$$

Now

$$\log K_{X,A} = \rho_A\sigma_X + \log K_{HA} \qquad (7)$$

$$\log K_{HA} = \upsilon_H\eta_A + \log K_{HA}{}^\circ \qquad (8)$$

Then

$$\rho_A = p\eta_A + \rho_A{}^\circ \qquad (9)$$

The electrical effect of a substituent may be written

$$\sigma_X = \lambda\sigma_I + \delta\sigma_R \qquad (10)$$

Defining $\lambda \equiv 1$

$$\sigma_X = \sigma_I + \delta\sigma_R \qquad (11)$$

Then from eq 1

$$Q_X = \rho\sigma_I + \rho\delta_R + Q_H \qquad (12)$$

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[8] M. Charton, *J. Am. Chem. Soc.*, **86**, 2033 (1964).

[9] M. Charton, unpublished results.

[10] S. I. Miller, *J. Am. Chem. Soc.*, **81**, 161 (1959).

which is equivalent to eq 2 with $\rho = \alpha$ and $\rho\delta = \beta$. Then ρ or α may be used as a measure of the magnitude of the electrical effect.

Sets 1B, 3, 5, and 9 permit a test of eq 9. The results obtained are $p = 0.773$, $\rho_A{}^\circ = 1.11$, $r = 0.973$, $s = 0.0906$, $s_p = 0.130$, and $t = 5.953$. The results show that this relationship apparently is obeyed. Unfortunately the limited number of values available does not provide a conclusive test. The data available do not permit any discussion of the variation of ρ with temperature or solvent.

It is of interest to compare the magnitude of electrical effects on charge-transfer complex formation with that of reactions of substituted benzenes. For electrophilic aromatic substitution[7] the value of ρ ranges from -2.4 to -12.1, while for hydrogen–deuterium exchange in the *para* position of substituted benzenes in liquid ammonia a ρ value of 5.6 is obtained.[11] The magnitude of ρ for charge-transfer complex formation in substituted benzenes is in general much smaller than the ρ values quoted above.

Steric Effects.—The peculiar effect of the isopropyl group in sets 11 and 13 is probably due to a steric effect. In the 1 position of naphthalene the isopropyl group is forced into a position in which its terminal methyl groups are above and below the plane of the naphthalene ring. This should prevent a close approach of donor and acceptor, and therefore decrease the value of the equilibrium constant. In the 2 position, the isopropyl group can adopt a conformation which places both methyl groups on one side of the plane of the ring, thus there is no steric effect for this group in the 2 position. A steric effect is observed for the tertiary butyl group in the 2 position (set 14), because any conformation of this group results in at least one terminal methyl group on each side of the ring. These conclusions are in accord with a number of observations reported in the literature of steric effects on complex formation.[3]

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[11] From a correlation of data reported by A. I. Shatenshtein, *Tetrahedron*, **18**, 95 (1962).

Application of the Hammett Equation to Substituent Effects on π Donors in Charge-Transfer Complex Formation. II. Multiply Substituted Donors

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Charge-transfer complex formation constants for 23 sets of $C_6H_{6-n}Me_n$ donors with halogen, SO_2, silver(I) ion, and π acceptors, one set of $C_6H_{6-n}Et_n$ donors with ICl as acceptor, and two sets of $C_6H_{6-n}F_n$ with I_2 as acceptor were successfully correlated with the Andrews–Keefer equation, $\log K_n = bn + d$. This equation may be derived from the extended Hammett equation for multiple substitution, $Q_{X_1 \ldots X_n} = \alpha\Sigma\sigma_{I,X} + \beta\Sigma\sigma_{R,X} + Q_H$ *if all positions in the benzene ring are equivalent with respect to charge-transfer complex formation.* The validity of the derivation is substantiated by the agreement between values of b calculated from appropriate α and β values obtained in previous work and the values of b obtained from the correlations. The importance of steric effects in polysubstituted benzenes is discussed. It is proposed that a statistical factor of 2 be applied to those polysubstituted benzene donors in which only one side of the benzene ring is capable of charge-transfer complex formation.

In the first paper of this series[1] we have examined substituent effects on charge-transfer complex formation in monosubstituted π donors. We now extend our studies to the problem of multiply substituted benzene π donors. Andrews and Keefer have proposed the equation

$$\log K_n = bn + d \tag{1}$$

for the correlation of complex formation constants of $C_6H_{6-n}R_n$ (R = alkyl). In the absence of steric effects a linear relationship is obtained.

We will approach this problem by means of the Hammett equation[2]

$$Q_X = \rho\sigma_X + Q_H \tag{2}$$

which in its extended form is

$$Q_X = \alpha\sigma_I + \beta\sigma_R + Q_H \tag{3}$$

To a reasonable approximation, the effect of several substituents may be expressed by the relationship

$$Q_{X_1 \ldots X_n} = \rho\Sigma\sigma_{X_i} + Q_H \tag{4}$$

where

$$\Sigma\sigma_{X_i} = \sigma_{X_1} + \sigma_{X_2} + \ldots \sigma_{X_n} \tag{5}$$

Applied to the extended form of the Hammett equation (eq 3) this relationship takes the form

$$Q_{X_1 \ldots X_n} = \alpha\Sigma\sigma_{I,X_i} + \beta\Sigma\sigma_{R,X_i} + Q_H \tag{6}$$

where

$$\Sigma\sigma_I = \sigma_{I,X_1} + \sigma_{I,X_2} + \ldots \sigma_{I,X_n} \tag{7}$$

$$\Sigma\sigma_R = \sigma_{R,X_1} + \sigma_{R,X_2} + \ldots \sigma_{R,X_n} \tag{7}$$

If the substituents present are identical and are situated in equivalent positions

$$\sigma_{I,X_1} = \sigma_{I,X_2} = \sigma_{I,X_n};\ \sigma_{R,X_1} = \sigma_{R,X_2} = \sigma_{R,X_n} \tag{8}$$

and

$$\Sigma\sigma_{I,X_i} = n\sigma_{I,X};\ \Sigma\sigma_{R,X} = n\sigma_{R,X} \tag{9}$$

giving

$$Q_{X_i \ldots X_n} = \alpha n\sigma_{I,X} + \beta n\sigma_{R,X} + Q_H \tag{10}$$

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[1] M. Charton, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, p 31–D; *J. Org. Chem.*, **31**, 2991 (1966).

[2] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 565; V. Palm, *Russ. Chem. Rev.*, **31**, 471 (1961); P. R. Wells, *Chem. Rev.*, **63**, 171 (1963); C. D. Ritchie and W. F. Sager, Jr., *Progr. Phys. Org. Chem.*, **2**, 323 (1963).