Infrared Intensities as a Quantitative Measure of Intermolecular Interactions. Part XX.[1] The Electronic Nature of Amino-, Ammonio-, and Diazonio-substituents

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Infrared intensities of series of *meta*-disubstituted benzenes show that the ND_3^+ and NMe_3^+ substituents are resonance donors. This is substantiated by the *para*-compounds; however, NMe_3^+ is a polarizable group. The diazonio-group N_2^+ is a strong acceptor substituent. The twisted NR_2 group is a resonance donor of strength comparable to $CHMe_2$.

THE resonance donor effect of the ammonio- and substituted ammonio-groups has not been widely recognized, although it is clearly indicated[2] by infrared intensities of *para*-disubstituted compounds $XC_6H_4NH_3^+$ and $XC_6H_4NMe_3^+$, and is suggested by other physical and chemical evidence (for a summary † see ref. 2). We now present further evidence for this resonance donor effect by NR_3^+ (R = H or Me), together with an estimate of the acceptance power of diazonio-group N_2^+ and a study of the donor properties of the *twisted* NR_2 group and its conjugate acid, using equations (1)—(3) which

$$A_{\nu 16} = 17{,}600\,(\sigma_R{}^{\circ})^2 + 100 \quad (1)$$
mono-Ph

$$A_{\nu 16} = 11{,}800\,(\sigma_R{}^{\circ}X - \sigma_R{}^{\circ}Y + \lambda)^2 + 170 \quad (2)$$
para-Ph

$$A_{\nu 16} = 19{,}000\,[(\sigma_R{}^{\circ}X)^2 + (\sigma_R{}^{\circ}Y)^2 + \sigma_R{}^{\circ}X\sigma_R{}^{\circ}Y] + 340 \quad (3)$$
meta-Ph

relate the infrared intensities of ν_{16} in mono-,[3] *para*-di-,[2] and *meta*-di-substituted benzenes.[4]

TABLE 1

Monosubstituted benzene cationic compounds

			1600[b]				1500	
Substituent	Solvent	$\pm\sigma_R{}^{\circ}$ [a]	ν	ε_A [c]	A [d]	ε [e]	ν	ε_A [c]
$\overset{+}{N}D_3Cl^-$	D_2O [f]	0·183	1605	77	689		1500	130
	D_2O [g]	0·189	1603	86	729	230	1499	134
	Me_2SO	0·332	1601	540	2040	4870	1496	609
$\overset{+}{N}Me_3Cl^-$	D_2O [f]	0·149	1599	28	490		1495	165
	D_2O	0·138	1596	29	435		1489	189
$\overset{+}{N}Me_3I^-$	Me_2SO	0·145	1594	24	470	340		
$N_2{}^+BF_4{}^-$	D_2O [f]	0·304	1591	128	1726			
	Me_2SO	0·290	1570 [h]	146	1550	1020		

[a] Of substituent from ref. 3. [b] None of these compounds show a resolved band near 1580 cm^{-1}. [c] Peak extinction coefficient. $\varepsilon_A = a_{max.}/cl$ where $a_{max.}$ is the absorbance at peak maximum, c is the concentration in mol per litre and l is the cell length in cm. [d] The integrated intensity of the 1600 and 1585 cm^{-1} bands. [e] ε is an estimate of the integrated intensity given by $\varepsilon = \varepsilon_A\Delta\nu^{\frac{1}{2}}$ where $\Delta\nu^{\frac{1}{2}}$ is the half-height line width. [f] Taken from ref. 3. [g] Measured in calcium fluoride cells (present work). [h] Ref. 6 gives ν_{16a} = 1570 in 50% aqueous HCl.

EXPERIMENTAL

Compounds were obtained commercially or prepared by known methods. Purities were checked by gas chromatography or melting points. Anilines were *N*-deuteriated as before.[3] Spectra were obtained on a Perkin-Elmer 125 spectrophotometer under conditions similar to those previously specified.[5] Dimethyl sulphoxide was distilled from calcium hydride and stored over molecular sieves (4A) AnalaR sodium chloride was dried under vacuum for 2 days at 225 °C. Other solvents were purified as before. Intensity area A values quoted are averages of four readings usually on two separate solutions; reproducibility of $A^{\frac{1}{2}}$ was ±1 unit in non-polar solvents or in deuterium oxide using calcium fluoride cells. Most compounds containing cationic groups were run either in deuterium oxide using Irtran cells as previously[2] or in sodium chloride-saturated dimethyl sulphoxide in sodium chloride cells. Reproducibility of $A^{\frac{1}{2}}$ in both cases is ±4 units.

RESULTS AND DISCUSSION

The Ammonio-substituents ND_3^+.—The infrared intensities of the relevant monosubstituted benzene[3] indicate

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† See also G. R. Wiley and S. I. Miller, *J. Org. Chem.*, 1972, **37**, 767, for evidence that the trimethylammonium group affects chemical shifts *via* a resonance mechanism.

[1] Part XIX, N. C. Cutress, A. R. Katritzky, C. Eaborn, and R. D. Topsom, *J. Organometallic Chem.*, 1972, **43**, 131.

[2] P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1968, **90**, 1767.

[3] R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1968, **90**, 1757.

[4] A. R. Katritzky, M. V. Sinnott, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1969, **91**, 628.

[5] R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1966, **88**, 1413.

[6] R. H. Nuttall, E. R. Roberts, and D. W. A. Sharp, *Spectrochim. Acta*, 1961, **17**, 947.

$\sigma_R^\circ \pm 0{\cdot}18$ for ND_3^+ and $\pm 0{\cdot}47$ for ND_2: the signs were deduced to be negative in both cases from intensity measurements of a series of *para*-disubstituted compounds.[2] Remeasurement of $PhND_3^+Cl^-$ now gives $\sigma_R^\circ \pm 0{\cdot}19$ for ND_3^+ in D_2O solution in good agreement with the previous result, but a high apparent value in Me_2SO (Table 1). We believe this high value to be spurious and to be due to free aniline formed by partial dissociation of the hydrochloride in dimethyl sulphoxide. This dissociation is confirmed by the ultraviolet spectrum of aniline hydrochloride in Me_2SO.

TABLE 2

meta-Disubstituted benzene cationic compounds

Substituents		Solvent	σ_R° [a]	ν(cm^{-1})		ε_A [b]		A [c]	R_m [d]	f_m [e]
				16a	16b	16a	16b			
$ND_3^+Cl^-$	Me	D_2O	−0·10	1618	1600	79	73	1530	0·25	0·25
	Cl	D_2O	−0·22	1602		174		2440	0·33	0·36
	Br	D_2O	−0·23	1600	1594	71	81	2720	0·35	0·36
	F	D_2O	−0·34	1615		182		4330	0·46	0·46
	OMe	D_2O	−0·43	1617	1604	160	121	5500	0·52	0·55
	NO_2 [f]	D_2O	+0·17	1602	1622	6	16	470	0·08	0·18
	CF_3 [f]	D_2O	+0·11	1612	1622	23	10	225	0·00	0·16
	CO_2Me	D_2O	+0·16	1614	1599	17	117	1400	0·24	0·08 → 0·25 [g]
ND_2	Me	CCl_4	−0·10	1614	1592	184	97	5180	0·51	0·53
	Cl	$CC]_4$	−0·22	1605	1580	331	60	7130	0·60	0·61
	Br	CCl_4	−0·23	1603	1569	159	48	7570	0·62	0·62
	F	CCl_4	−0·34	1625 1611	1588	163	127 117	8890	0·67	0·71
	NO_2	CCl_4	+0·17	1609	1588	84	28	2780	0·36	0·41
$NMe_3^+Cl^-$	Me	D_2O	−0·10	1616	1591	40	23	1530	0·25	0·22
	Cl	Me_2SO	−0·22	1590		106		2230	0·32	0·32
	F	D_2O	−0·34	1612		256		4620	0·48	0·44
	OMe	D_2O	−0·43	1613	1595			7000	0·59	0·52
	NMe_3^+	D_2O	−0·15	1607		28		2860	0·36	0·15
$N_2^+BF_4^-$	F	Me_2SO	−0·34	1596	1588 1580	148		2400	0·33	0·32
	Br	Me_2SO	−0·23	1576	1556	51	36	1670	0·26	0·26
	Cl	Me_2SO	−0·22	1578	1560	49	41	1460	0·25	0·26
	NO_2	Me_2SO	+0·17	1598	1590	199		3995	0·44	0·40
	CF_3	Me_2SO	+0·11	1604	1570	41	74	2115	0·31	0·36

[a] Of substituent from ref. 3. [b] Peak extinction coefficient. $\varepsilon_A = a_{max.}/cl$, where $a_{max.}$ is absorbance at peak maximum, c is concentration in mol per litre and l is cell length in cm. [c] The integrated intensity of the 1600 and 1585 cm^{-1} bands. [d] $R_m = [(A - 340)/19{,}000]^{\frac{1}{2}}$. [e] $f_m = [\sigma_R^\circ 1^2 + \sigma_R^\circ 2^2 + \sigma_R^\circ 1 \sigma_R^\circ 2]^{\frac{1}{2}}$. [f] Measured in calcium fluoride cells. [g] Range arises from asymmetry of CO_2Me substituent (see ref. 4).

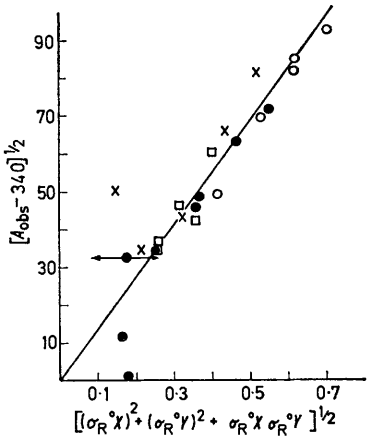

FIGURE 1 $[A_{obs} - 340]^{\frac{1}{2}}$ plotted against $[(\sigma_R^\circ X)^2 + (\sigma_R^\circ Y)^2 + \sigma_R^\circ X \sigma_R^\circ Y]^{\frac{1}{2}}$ for *meta*-X·C_6H_4·Y: for Y = ND_3^+ (●) with σ_R° taken as −0·19; for Y = ND_2 (○) with σ_R° taken as −0·47; for Y = NMe_3^+ (×) with σ_R° taken as −0·15; for Y = N_2^+ (□) with σ_R° taken as +0·29. The line drawn has slope $(19{,}000)^{\frac{1}{2}}$ of equation (3)

Results now obtained for *meta*-disubstituted derivatives $XC_6H_4ND_3^+$ and $XC_6H_4ND_2$ (Table 2) are plotted in Figure 1; clearly they are in good agreement with ND_3^+ acting as a *donor* substituent. Figure 2 shows the assumption of acceptor behaviour for ND_3^+ does not yield an acceptable relation. The results of Table 2

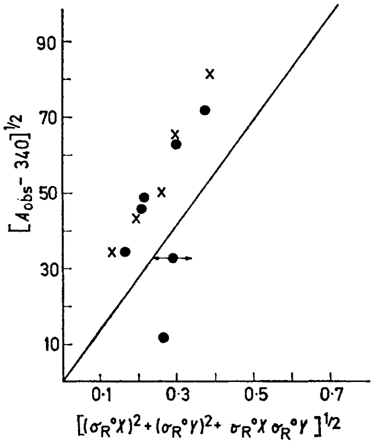

FIGURE 2 $[A_{obs} - 340]^{\frac{1}{2}}$ plotted against $[(\sigma_R^\circ X)^2 + (\sigma_R^\circ Y)^2 + \sigma_R^\circ X \sigma_R^\circ Y]^{\frac{1}{2}}$ for *meta*-X·C_6H_4·Y: for Y = ND_3^+ (●) with σ_R° taken as +0·19; for Y = NMe_3^+ (×) with σ_R° taken as +0·15. The line drawn has slope $(19{,}000)^{\frac{1}{2}}$ of equation (3) and Figure 1 also clearly confirm the donor properties of ND_2, as expected.

The Trimethylammonio-substituent NMe_3^+.—For the monosubstituted benzene $PhNMe_3^+Cl^-$, the previous results in D_2O and the present results in D_2O and Me_2SO all give $\sigma_R^\circ \pm 0{\cdot}144 \pm 0{\cdot}005$. No dissociation is expected for this compound, and there is evidently little solvent effect. The results for the *meta*-disubstituted derivatives $XC_6H_4NMe_3^+$ (Table 2) plotted in Figures 1 and 2 clearly confirm the resonance donor character of the NMe_3^+ group with $\sigma_R^\circ = -0{\cdot}14$.

TABLE 3

para-Disubstituted benzene cationic compounds (dimethyl sulphoxide solutions)

Substituent		σ_R° [a]	1600				A [c]	R_p [d]	f_p	
			ν		ε_A [b]					
			16a	16b	16a	16b			e	f
$NMe_3^+I^-$	NMe_2	$-0{\cdot}53$	1605		237		5000	0·64	$-0{\cdot}38$	
	OMe	$-0{\cdot}43$	1606	1593	85	89	1950	0·39	$-0{\cdot}28$	
	OEt	$-0{\cdot}44$	1607	1591	81	80	1970	0·39	$-0{\cdot}29$	
	F [g]	$-0{\cdot}34$	1606				830	0·24	$-0{\cdot}19$	
	Me	$-0{\cdot}10$	1604	1590	4	7	133	0·00	$+0{\cdot}05$	
	NO_2 [g]	$+0{\cdot}17$	1622	1598			1500	0·34	0·32	
N_2^+,BF_4^-	NMe_2	$-0{\cdot}53$	1592		2340		33,780	1·69	0·82	1·68
	OMe	$-0{\cdot}43$	1582		1150		17,215	1·20	0·72	1·22
	F	$-0{\cdot}34$	1578		661		6920	0·76	0·63	0·76
	Cl	$-0{\cdot}22$	1561		450		4950	0·64	0·51	0·63
	Me	$-0{\cdot}10$	1581		371		3970	0·57	0·39	0·53
	NO_2	$+0{\cdot}17$	1610		63		1295	0·31	0·12	

[a] Of substituent from ref. 3. [b] Peak extinction coefficient. $\varepsilon_A = a_{max.}/cl$ where $a_{max.}$ is absorbance at peak maximum, c is concentration in mol per litre and l is cell length in cm. [c] The integrated intensity of the 1600 and 1585 cm^{-1} band. [d] $R_p = [(A - 170)/11{,}800]^{\frac{1}{2}}$. [e] $f_p = \sigma_R^\circ 1 - \sigma_R^\circ 2$. [f] $f_p = [\sigma_R^\circ 1 - \sigma_R^\circ 2 + K_X\sigma_R^\circ 1]$ for d orbital acceptors or $= [\sigma_R^\circ 1 - \sigma_R^\circ 2 + K_A(\sigma^+ - \sigma)]$ for acceptor groups. [g] Measured by P. J. Q. English using D_2O on NMe_3^+,Cl^-.

We have now examined a wider range of *para*-disubstituted derivatives ($XC_6H_4NMe_3^+$) with the results summarized in Table 3. Although the results for the *para*-substituents F, Me, and NO_2 are in good agreement with those predicted, for the strong donor substituents OMe, OEt, and NMe_2, a higher intensity is observed than expected. This is probably due to the considerable polarizability of the bulky NMe_3^+ group, and is similar to the results found for the CMe_3 compounds.[7]

The Diazonio-substituent N_2^+.—From $PhN_2^+BF_4^-$ in Me_2SO we calculate σ_R° for N_2^+ as $+0{\cdot}29$, in good agreement with the previous [3] value of $+0{\cdot}30$ deduced from $PhN_2^+BF_4^-$ measured in D_2O. Difficulty was experienced with the substituted diazonium cations: in the *meta*-series the Me and NMe_2 compounds decomposed obviously during preparation or measurement, however, satisfactory results were obtained for five compounds (Table 2). Good agreement is found with equation (3), as shown in Figure 1.

In the *para*-series, only derivatives with electron-donor substituents were stable. A plot of $(A_{obs} - 170)^{\frac{1}{2}}$ against ($\sigma_R^\circ 1$ or $\sigma_R^\circ 2$) showed large discrepancies from the line of slope 11,800, indicative of strong conjugative interaction (Figure 3); however, use of the previously justified [2] correction factor $K_X\sigma_R^\circ D$ in $[\sigma_R^\circ 1 - \sigma_R^\circ 2 + K_X\sigma_R^\circ D]$ with $K(N_2^+) = 0{\cdot}99$ gave an excellent correlation (Figure 3). The large magnitude of $K(N_2^+)$ reflects the strong acceptor power of this substituent: this acceptor power is underlined by the exalted value of σ_R° deduced from ^{19}F measurements [8] of $+0{\cdot}65$ which includes direct resonance interaction between the substituents in *p*-fluorodiazonium cation: [2] however, the discrepancy is only partly explained by the factor [2] $0{\cdot}5\,K_A$ $(\sigma^+ - \sigma)$ of $0{\cdot}17$.

$$A_{N_2^+}^{\frac{1}{2}} = +45{\cdot}57 - 163{\cdot}8\,(\sigma^+ - \sigma) \qquad (4)$$

$$\nu_{N^+\equiv N} = 131{\cdot}6\,(\sigma^+ - \sigma) + 2294 \qquad (5)$$

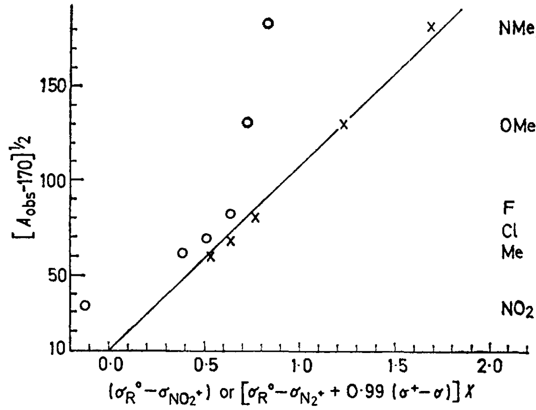

FIGURE 3 $[A_{obs} - 170]^{\frac{1}{2}}$ for *para*-substituted diazonium fluoroborates plotted against (a) $[\sigma_R^\circ X - 0{\cdot}29]$ (○) and (b) $[\sigma_R^\circ X - 0{\cdot}29 + 0{\cdot}99\ (\sigma^+ - \sigma)]$ (×). The line drawn has slope $(11{,}800)^{\frac{1}{2}}$ of equation (2)

We have also found that the intensities and frequencies of the ν(N≡N) bands for the substituted diazonium cations (Table 4) are correlated by equations (4) and (5);

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[7] T. J. Broxton, L. W. Deady, A. R. Katritzky, A. Liu, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1970, **92**, 6845.

[8] R. W. Taft and W. A. Sheppard, personal communication, referred to in ref. 3.

Table 4

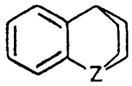
Benzene diazonium νN≡N frequencies and intensities [a]

Substituent	2200 ν	2200 ε_A [b]	A [c]	$\sigma^+ - \sigma$ [d]
p-NMe_2	2165	675	41,000	−0·87
p-OMe	2247	245	11,750	−0·51
p-F	2282	131	3775	−0·13
p-Cl	2286	147	4050	−0·12
p-Me	2270	185	5920	−0·14
p-NO_2	2302	64	1470	+0·01
m-F	2295	81	2210	+0·01
m-Br	2293	94	2218	+0·01
m-Cl	2295	93	9460	+0·03
m-NO_2	2294	44	1215	−0·04
m-CF_3	2292	61	1700	0·09
H	2286	104	2530	0·00

[a] In Me_2SO. [b] ε_A is the peak extinction coefficient. $\varepsilon_A = a_{max.}/cl$ where $a_{max.}$ is maximum peak absorbance, c is concentration in mol per litre and l is the cell length in cm. [c] Integrated intensity $A = \Sigma a_{max}/_{cl}$. [d] Taken from C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 334.

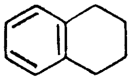
the correlation coefficients ($r = 0{\cdot}973$ and $0{\cdot}965$ respectively) are significantly better than that for similar treatment using σ^+ and much better than that using σ alone. Previous evidence [9] suggests that vibrational frequencies of groups capable of conjugative electron withdrawal follow σ^+, but the frequency and intensity of $\nu(N_2^+)$ evidently require an enhanced σ^+ value. Previous work by Whetsel [10] and by Nuttall [6] did not lead to a clear-cut relation for ν or A. Kazitsyna [11] first related frequency and σ using σ^+ for strong donors but later [12] used σ^+ for all substituents. For ν(N≡N) intensity, Kazitsyna [11] claimed the relation log $A \propto \sigma^+$. However, while Kazitsyna's values are slightly larger than those obtained here, they are linearly related by the factor 1·12 ($r = 0{\cdot}997$). Thus it appears that while the intensities are solvent dependent, the intramolecular electronic interactions are proportional in Me_2SO and MeOH.

The Twisted NR_2-*substituent.*—The correlation of the infrared intensities of *ortho*-disubstituted benzenes with $\sigma_R°$ values [4] is less precise than for the *meta*- and *para*-analogues. However, the overall similarity in the A values of quinuclidine (1) and quinuclidine cation (2) with tetralin (3) (Table 5) suggests that CH_3, NH_3^+, and NH_2 (twisted so that the lone pair is orthogonal to the π-system of the benzene ring) are all resonance donors of the same order of magnitude. This overall similarity suggests equivalent mechanisms of electron donation from each of these seemingly dissimilar groups.



(1) Z = N

(2) Z = NH^+



(3)

Table 5

ortho-Disubstituted benzene cationic compounds

Compound	Solvent	1600 ν	1600 ε_A [a]	1585 ν	1585 ε_A [a]	A [b]
Tetralin	CCl_4 [c]	1601	7	1579	10	210
Benzoquinuclidine	CCl_4 [c]	1623	4	1585	5	250
		1605	14			
Benzoquinuclidine deuteriobromide	Me_2SO	1615	10	1595	7	200

[a] Peak extinction coefficient as in Table 2. [b] The integrated intensity of the 1600 and 1585 cm^{-1} band. [c] Containing 10% benzene.

$$A_{\nu 16 \atop ortho\text{-}Ph} = 15{,}900\,\{(\sigma_R°1)^2 + (\sigma_R°2)^2 - \sigma_R°1\sigma_R°2\} \quad (6)$$

Equation (6), derived for *ortho*-disubstituted benzenes,[4] indicates for tetralin a $\sigma_R°$ of −0·115 for each substituent in good agreement with the value [3] for n-propyl of −0·109. For benzoquinuclidine, assuming $\sigma_R°$ for the $\cdot CH(CH_2\cdot)_2$ group is −0·115 (*cf.* isopropyl −0·115 [3]), gives $\sigma_R°$ for $\cdot N(CH_2\cdot)_2$ of −0·134 using equation (6); and a similar calculation gives $\cdot\overset{+}{N}D(CH_2\cdot)_2$ of −0·109.

Conclusions.—The results show clearly that ND_3^+ and NMe_3^+ are resonance donors of comparable magnitude to alkyl groups, while N_2^+ is a powerful resonance electron acceptor. Further, an NR_2 group, twisted orthogonally to the benzene ring plane still possesses resonance donor properties equivalent to an alkyl group.

The mechanism of electron donation is similar to that operating in the alkyl groups CH_3, CMe_3. Evidently any π-inductive effect of the integral charge is small in these compounds.

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[9] A. R. Katritzky and R. D. Topsom, in ' Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, forthcoming.

[10] K. B. Whetsel, G. F. Hawkins, and F. E. Johnson, *J. Amer. Chem. Soc.*, 1956, **78**, 3360.

[11] L. A. Kazitsyna, B. S. Kikot', L. D. Ashkinadze, and O. A. Reutov, *Doklady Akad. Nauk S.S.S.R.*, 1963, **151**, 573.

[12] L. A. Kazitsyna, L. D. Ashkinadze, and O. A. Reutov, *Bull. Acad. Sci. U.S.S.R.*, 1967, 685.