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B13

TK 42.083

1972
international book year



161 ETK 1356

KFKI-72-58

Á. I. Kiss

J. Szóke

QUANTUMSPECTROSCOPY

**N° 4. Pi-electron SCF-MO calculations
for disubstituted benzene derivatives
containing two donor groups**

Hungarian Academy of Sciences

**CENTRAL
RESEARCH
INSTITUTE FOR
PHYSICS**



BUDAPEST

QUANTUMSPECTROSCOPY

Papers in this series:

1. A.I.Kiss and J.Szöke: Pi-Electron SCF-MO Calculations for Monosubstituted Derivatives of Benzene
Chem.Phys.Lett. 11, 52 /1971/ and KFKI-72-1
2. A.I.Kiss and J.Szöke: Theoretical Investigation of Electronic Spectra of Monosubstituted Benzene Derivatives
Hung.Chem.Acta 1972, 74, 33 and KFKI-72-2
3. A.I.Kiss and J.Szöke: Pi-Electron SCF-MO Calculations for Distributed Benzene Derivatives Containing Two Donor Groups
Part one: Discussion of Results.
Submitted to Chem.Phys.Lett.
4. A.I.Kiss and J.Szöke: Pi-Electron SCF-MO Calculations for Distributed Benzene Derivatives Containing Two Donor Groups
Part two: Numerical Results of Calculations
KFKI-72-58
5. J.Szöke: Energy Conversation Tables for Quantum Spectroscopy
/in preparation/

Pi-ELECTRON SCF-MO CALCULATIONS FOR DISUBSTITUTED
BENZENE DERIVATIVES CONTAINING TWO DONOR GROUPS

Part Two:
Numerical Results of Calculations

A.I.Kiss

Department of Physical Chemistry
Technical University, Budapest, Hungary

and

J.Szőke

Department of Physical Chemistry
Technical University, Budapest, Hungary

and

Physical Optics Department
Central Research Institute for Physics, Budapest, Hungary

ABSTRACT

Part one of this paper, containing a discussion of the calculation results, is to be published in Chem.Phys.Letters. The complete results of interest from the point of view of the spectra-structure correlations - which had to be omitted in the previous paper because of space limitations - are reported here in detail.

РЕЗЮМЕ

В настоящей работе, первая часть которой представляет собой дискуссию результатов измерения и будет опубликована в журнале "Chem. Phys. Lett.", сообщаются также и частичные результаты всех расчетов.

KIVONAT

A közlemény első része, amely a mérési eredményeket diszkutálja, a Chem.Phys.Lettersben jelenik meg. Ez a közlemény helyszüke miatt nem tartalmazza a számolási részeredményeket, amit a jelent reportban teszünk közzé, azok számára, akik az eredmények részletei iránt érdeklődnek.

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1. STARTING PARAMETERS USED IN THE PPP- CALCULATIONS

1.1 Atomic parameters /in eV/

	C	N	O	F	Cl
I_{μ}	11.16	25.73	30.07	34.00	24.37
$\gamma_{\mu\mu}$	11.13	16.76	19.24	21.39	13.03
A_{μ}	0.03	8.97	10.83	12.61	11.34

1.2 Bonding parameters

	γ_{C-x} (Å)	β_{C-x} (eV)
C-C	1.397	-2.39
C-NH ₂	1.38	-2.30
C-OH	1.36	-2.50
C-F	1.30	-2.20
C-Cl	1.69	-2.20

2. CALCULATED AND EXPERIMENTAL SPECTRAL DATA

Compound	Calculated			Experimental ^{a/}			Ref
	E (eV)	f	α	E (eV)	log ϵ	f	
Fluorobenzene	4.758	0.017	90.0	4.750	3.08	0.029	1
	5.929	0.111	0.0	6.107	3.88	0.182	
	6.836	1.028	270.0				
	6.837	1.163	0.0				
Chlorobenzene	4.717	0.022	90.0	4.678	2.43	0.006	1
	5.792	0.232	0.0	5.740	3.92	0.199	
	6.742	1.071	0.0	6.525	4.74	1.319	
	6.749	0.907	270.0	6.525	4.74	1.319	
Phenol	4.613	0.041	90.0	4.575	3.28	0.046	2
	5.703	0.252	0.0	5.876	3.72	0.126	
	6.675	0.808	270.0				
	6.758	1.066	0.0				
Aniline	4.379	0.060	90.0	4.305	3.27	0.044	2
	5.314	0.418	0.0	5.298	3.95	0.213	
	6.324	0.392	270.0				
	6.646	0.810	0.0				
O-Difluorobenzene	4.637	0.023	210.0				
	5.695	0.098	120.0				
	6.586	1.200	210.0				
	6.643	0.939	120.0				
M-Difluorobenzene	4.663	0.015	150.0	4.768	3.00	0.024	3
	5.792	0.053	60.0	6.107	3.90	0.192	
	6.573	1.257	150.0				
	6.632	0.972	240.0				
P-Difluorobenzene	4.576	0.055	90.0	4.643	3.48	0.072	3
	5.723	0.244	0.0	6.205	3.85	0.168	
	6.788	1.144	0.0				
	6.801	0.971	270.0				

	Calculated			Experimental ^{a)}			Ref
	E (eV)	f	α	E (eV)	log ϵ	f	
O-Fluorochlorobenzene	4.606	0.029	33.3	4.558	3.18	0.0360	3
	5.593	0.149	320.0	5.794	4.00	0.240	
	6.483	1.186	29.4				
	6.580	0.860	119.7				
M-Fluorochlorobenzene	4.635	0.017	143.9	4.558	3.00	0.024	3
	5.715	0.104	29.3	5.767	3.93	0.204	
	6.442	1.232	157.0				
	6.554	0.895	249.1				
P-Fluorochlorobenzene	4.539	0.060	90.0	4.476	3.06	0.028	3
	5.620	0.343	0.0	5.767	3.74	0.132	
	6.735	1.084	0.0				
	6.760	0.903	270.0				
O-Fluorophenol	4.515	0.044	229.3	4.609	3.20	0.038	3
	5.493	0.177	325.8	5.794	3.76	0.139	
	6.447	1.034	232.6				
	6.534	0.906	152.6				
M-Fluorophenol	4.559	0.028	305.6	4.600	3.16	0.035	3
	5.641	0.129	21.5	5.807	3.72	0.125	
	6.440	1.202	325.7				
	6.462	0.819	232.3				
P-Fluorophenol	4.423	0.081	270.0	4.404	3.49	0.074	3
	5.546	0.357	0.0	5.834	3.62	0.101	
	6.723	0.797	270.0				
	6.745	1.077	180.0				
O-Fluoroaniline	4.315	0.064	237.9	4.412	3.40	0.060	3
	5.153	0.311	341.4	5.390	4.04	0.264	
	6.151	0.578	249.9				
	6.410	0.844	175.8				
M-Fluoroaniline	4.375	0.043	295.1	4.381	3.28	0.046	3
	5.313	0.329	6.0	5.298	4.00	0.240	
	6.134	0.429	250.1				
	6.288	0.930	156.3				

	Calculated			Experimental a/			Ref
	E (eV)	f	α	E (eV)	log ϵ	f	
P-Fluoroaniline	4.200	0.094	270.0	4.189	3.34	0.053	3
	5.226	0.490	0.0	5.390	3.85	0.168	
	6.355	0.258	270.0				
	6.641	0.782	180.0				
O-Dichlorobenzene	4.576	0.036	210.0	4.592	2.54	0.008	4
	5.508	0.163	300.0	5.661	3.92	0.199	
	6.376	1.216	210.0				
	6.526	0.795	120.0				
M-Dichlorobenzene	4.610	0.020	150.0	4.592	2.57	0.009	4
	5.667	0.096	60.0	5.610	3.90	0.192	
	6.297	1.279	150.0				
	6.478	0.828	240.0				
P-Dichlorobenzene	4.505	0.065	90.0	4.541	2.70	0.012	4
	5.527	0.434	0.0	5.510	4.13	0.324	
	6.707	1.055	0.0				
	6.738	0.881	270.0				
O-Chlorophenol	4.489	0.052	226.3	4.525	3.37	0.056	4
	5.416	0.178	309.7	5.848	3.81	0.155	
	6.348	1.135	222.0				
	6.476	0.791	140.7				
M-Chlorophenol	4.539	0.029	310.6	4.525	3.31	0.049	4
	5.606	0.103	43.8	5.740	3.81	0.156	
	6.278	1.261	324.6				
	6.386	0.767	231.7				
P-Chlorophenol	4.392	0.085	270.0	4.412	3.27	0.044	4
	5.465	0.440	0.0	5.535	3.94	0.211	
	6.719	1.059	180.0				
	6.720	0.806	270.0				
O-Chloroaniline	4.296	0.072	235.5	4.261	3.46	0.070	
	5.104	0.281	333.1	5.253	3.94	0.209	
	6.088	0.697	239.9				
	6.333	0.791	171.6				

	Calculated			Experimental ^{a/}			Ref
	E (eV)	f	α	E (eV)	log ϵ	f	
M-Chloroaniline	4.366	0.043	298.5	4.290	3.32	0.050	4
	5.312	0.292	9.9	5.209	3.93	0.204	
	6.064	0.551	267.8				
	6.110	0.929	161.5				
P-Chloroaniline	4.178	0.097	270.0	4.174	3.28	0.046	4
	5.171	0.551	0.0	5.102	4.10	0.300	
	6.352	0.224	270.0				
	6.646	0.798	180.0				
O-Dihydroxybenzene	4.415	0.062	210.0	4.492	3.40	0.060	5
	5.315	0.193	300.0	5.767	3.83	0.163	
	6.330	1.162	210.0				
	6.393	0.688	120.0				
M-Dihydroxybenzene	4.485	0.032	150.0	4.500	3.33	0.052	5
	5.553	0.095	60.0	5.687	3.83	0.163	
	6.254	1.271	150.0				
	6.274	0.713	240.0				
P-Dihydroxybenzene	4.275	0.105	90.0	4.261	3.45	0.070	5
	5.406	0.450	0.0	5.535	3.64	0.106	
	6.727	1.061	0.0				
	6.729	0.779	270.0				
O-Aminophenol	4.245	0.081	79.4	4.275	3.52	0.079	5
	5.021	0.265	336.1	5.253	3.85	0.168	
	6.055	0.695	58.1				
	6.2435	0.785	185.4				
M-Aminophenol	4.340	0.041	285.6	4.335	3.36	0.055	5
	5.298	0.237	225.3	5.276	3.83	0.163	
	5.953	0.478	1.2				
	6.036	1.061	272.6				
P-Aminophenol	4.070	0.113	270.0	4.052	3.41	0.061	5
	5.137	0.558	180.0	5.253	3.85	0.172	
	6.324	0.116	90.0				
	6.642	0.749	180.0				

	Calculated			Experimental ^{a/}			Ref
	E eV	f	α	E eV	log ϵ	f	
O-Diaminobenzene	4.117	0.098	210.0	4.261	3.54	0.084	6
	4.805	0.254	300.0	5.242	3.82	0.158	
	5.929	1.036	210.0				
	5.932	0.315	120.0				
M-Diaminobenzene	4.239	0.043	330.0	4.203	3.42	0.062	6
	5.197	0.127	240.0	5.144	3.85	0.168	
	5.653	0.400	240.0				
	5.677	1.126	150.0				
P-Diaminobenzene	3.903	0.119	90.0	3.911	3.30	0.048	6
	4.949	0.642	0.0	5.019	3.93	0.204	
	6.010	0.000	30.0				
	6.507	0.000	92.2				
	6.526	0.473	270.0				
	6.659	0.905	0.0				

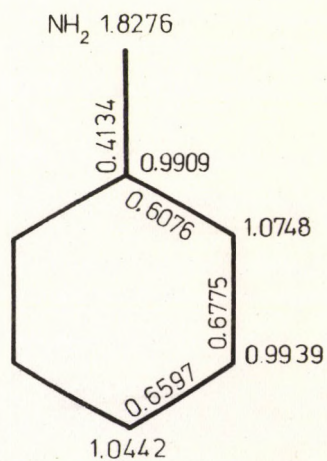
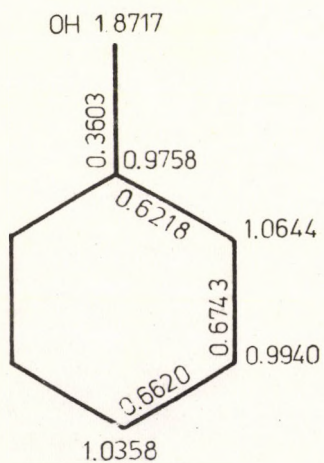
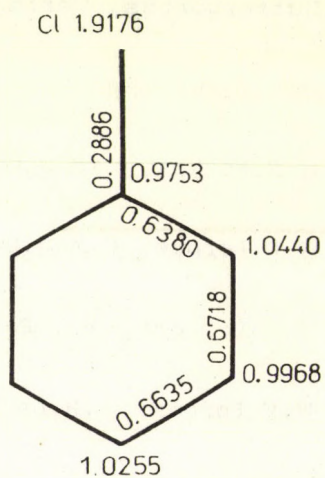
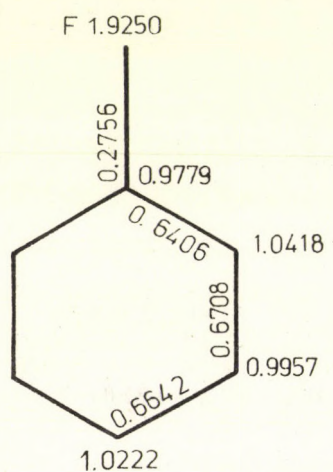
a/ The experimental data refer to cyclohexane solution.

3. REFERENCES

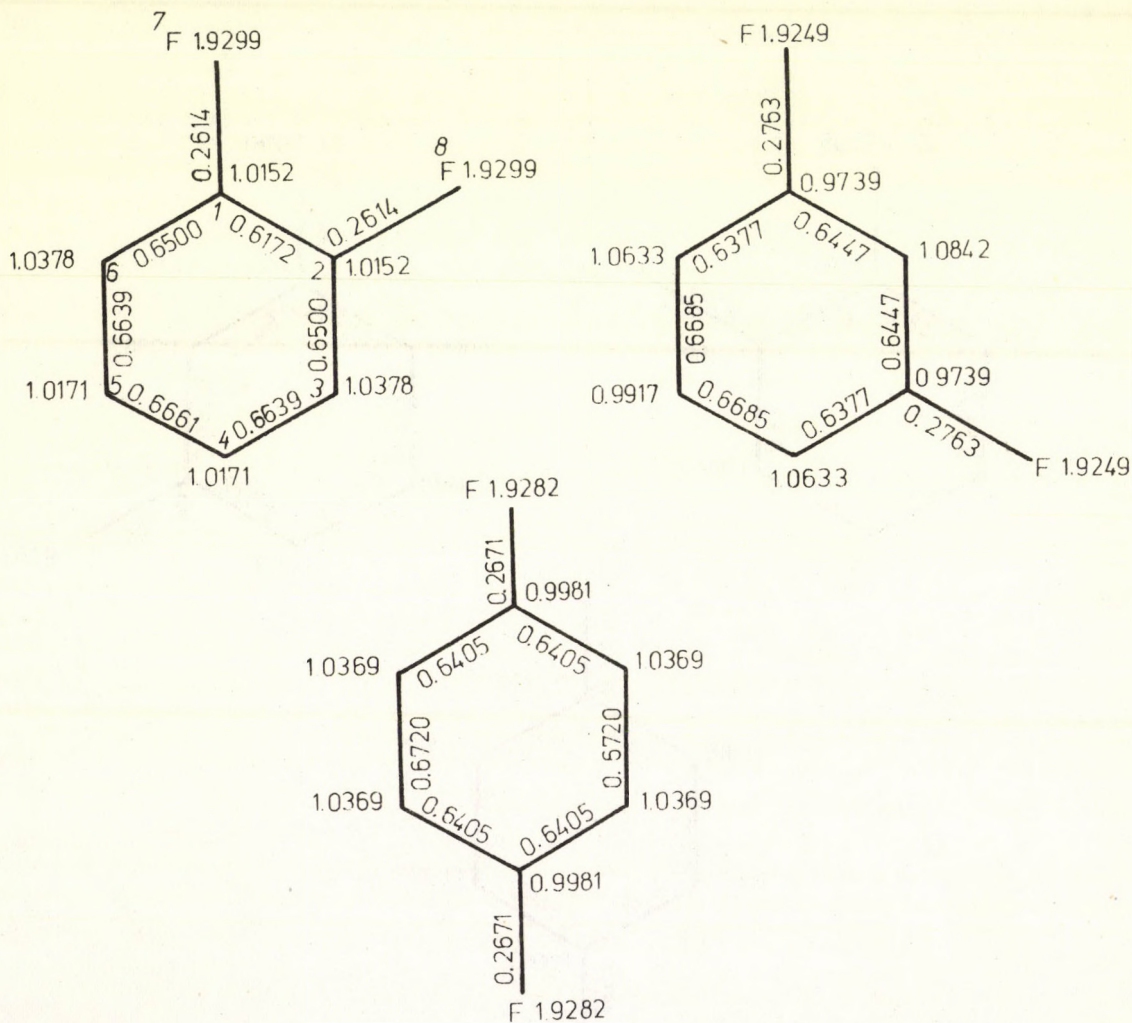
1. DMS UV Atlas of Organic Compounds, Vol. III-IV.
Butterworths, Verlag Chemie, 1967-68.
2. Own measurement
3. W.F.Forbes, Can.J.Chem. 37, 1977 /1959/
4. W.F.Forbes, Can.J.Chem. 38, 1104 /1960/
5. J.C.Dearden, W.F.Forbes, Can.J.Chem. 37, 1294 /1959/
6. W.F.Forbes, I.R.Leckie, Can.J.Chem. 36, 1371 /1958/

4. Pi- ELECTRON DENSITIES AND BOND ORDERS

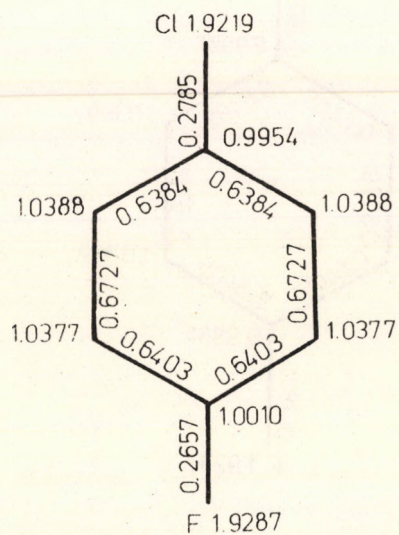
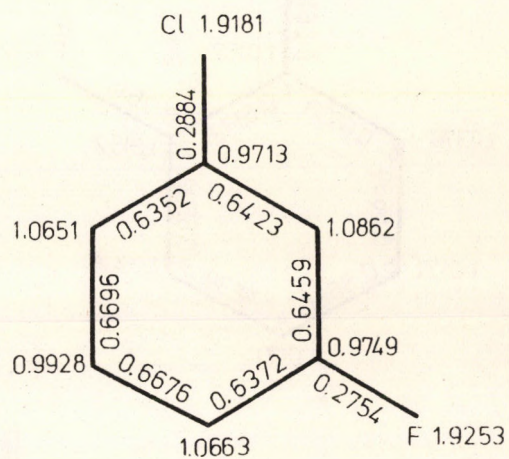
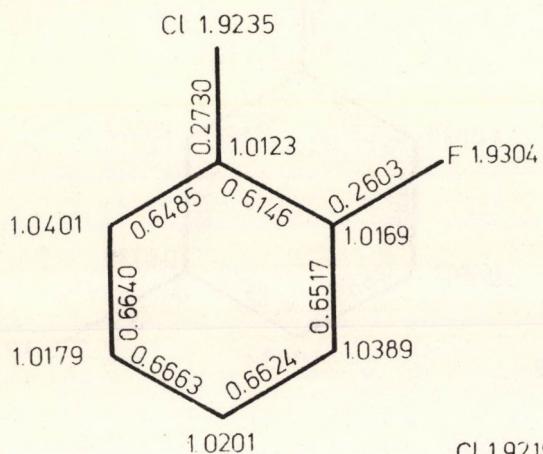
4.1. Monosubstituted Derivatives



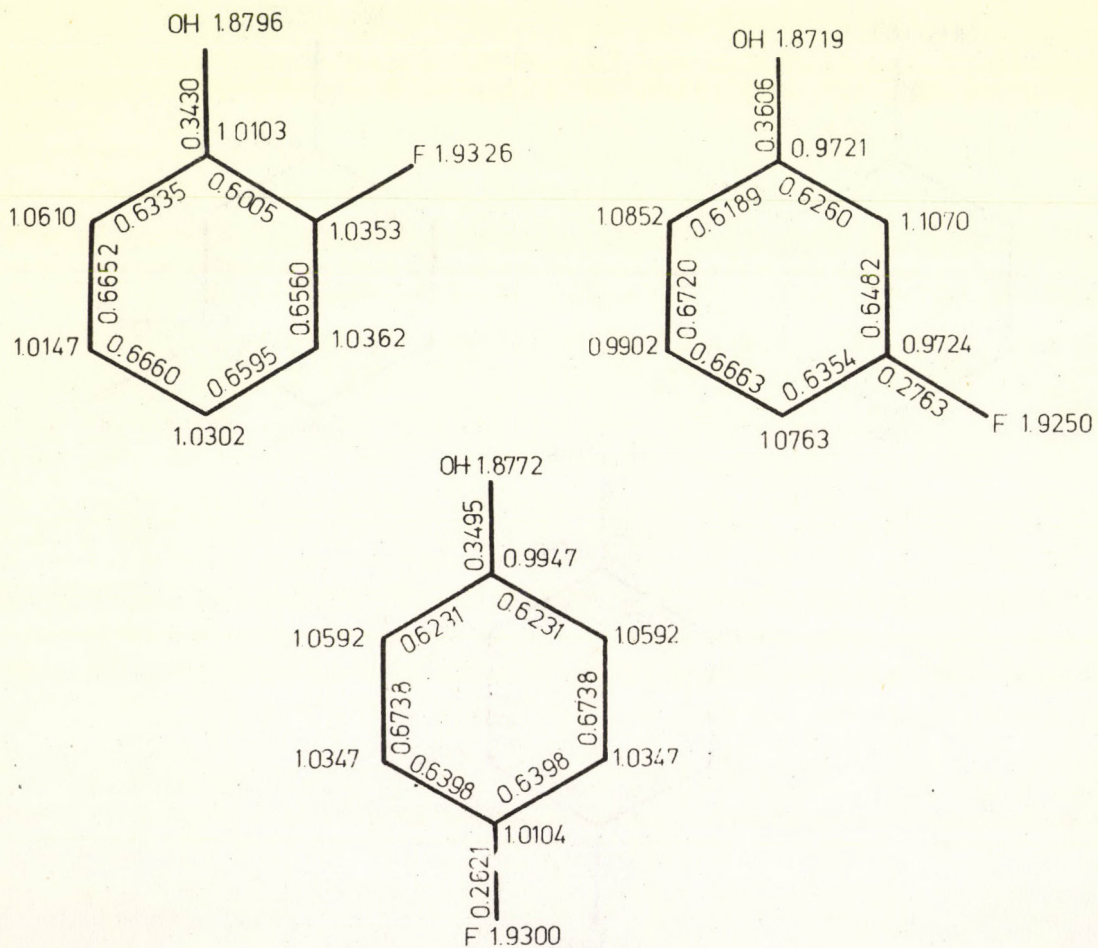
4.2 Di-fluoro Derivatives



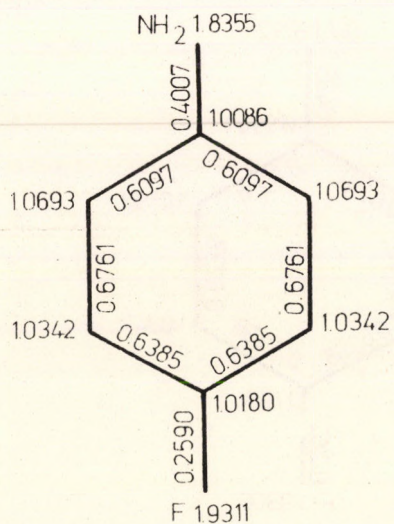
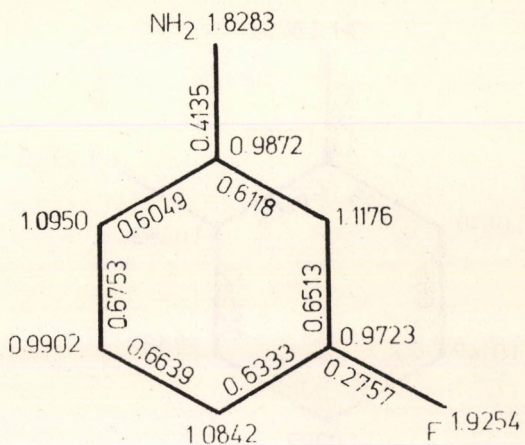
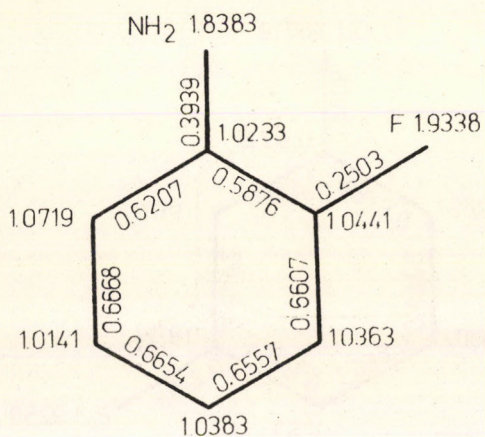
4.3 Fluoro-chloro Derivatives



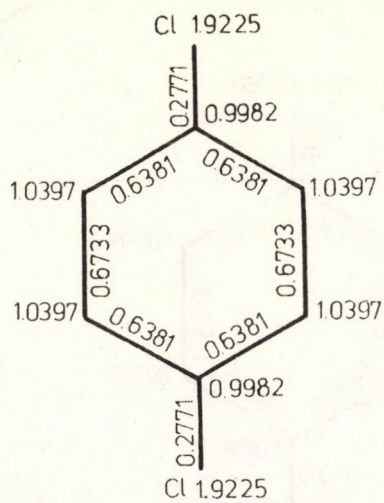
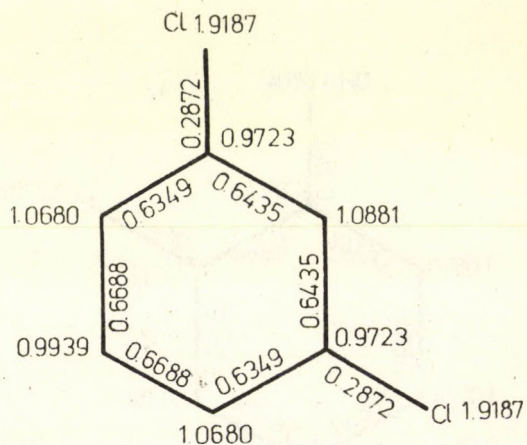
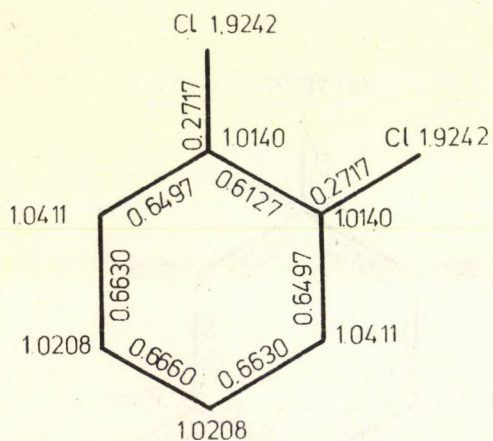
4.4 Hydroxy-fluoro Derivatives



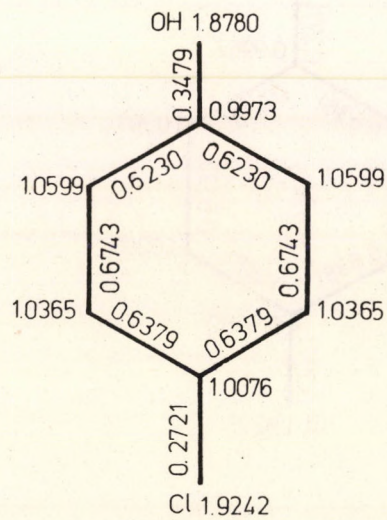
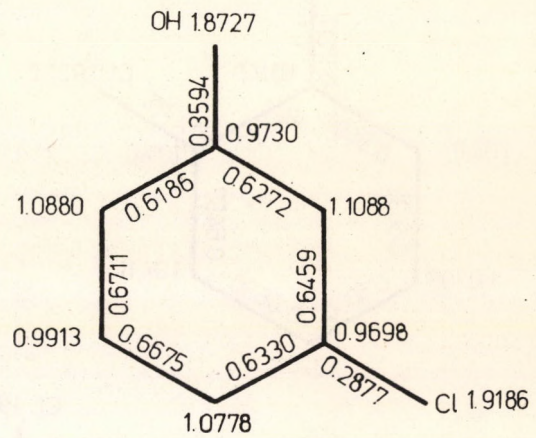
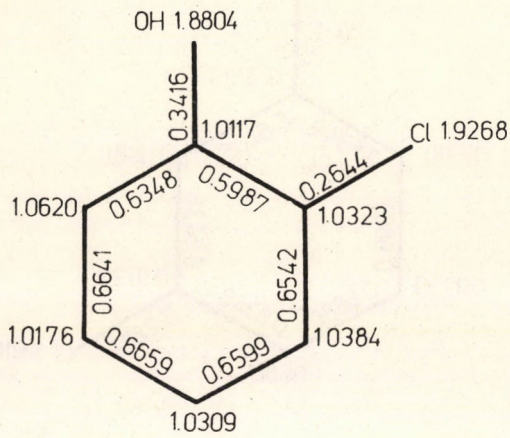
4.5 Amino-Fluor Derivatives



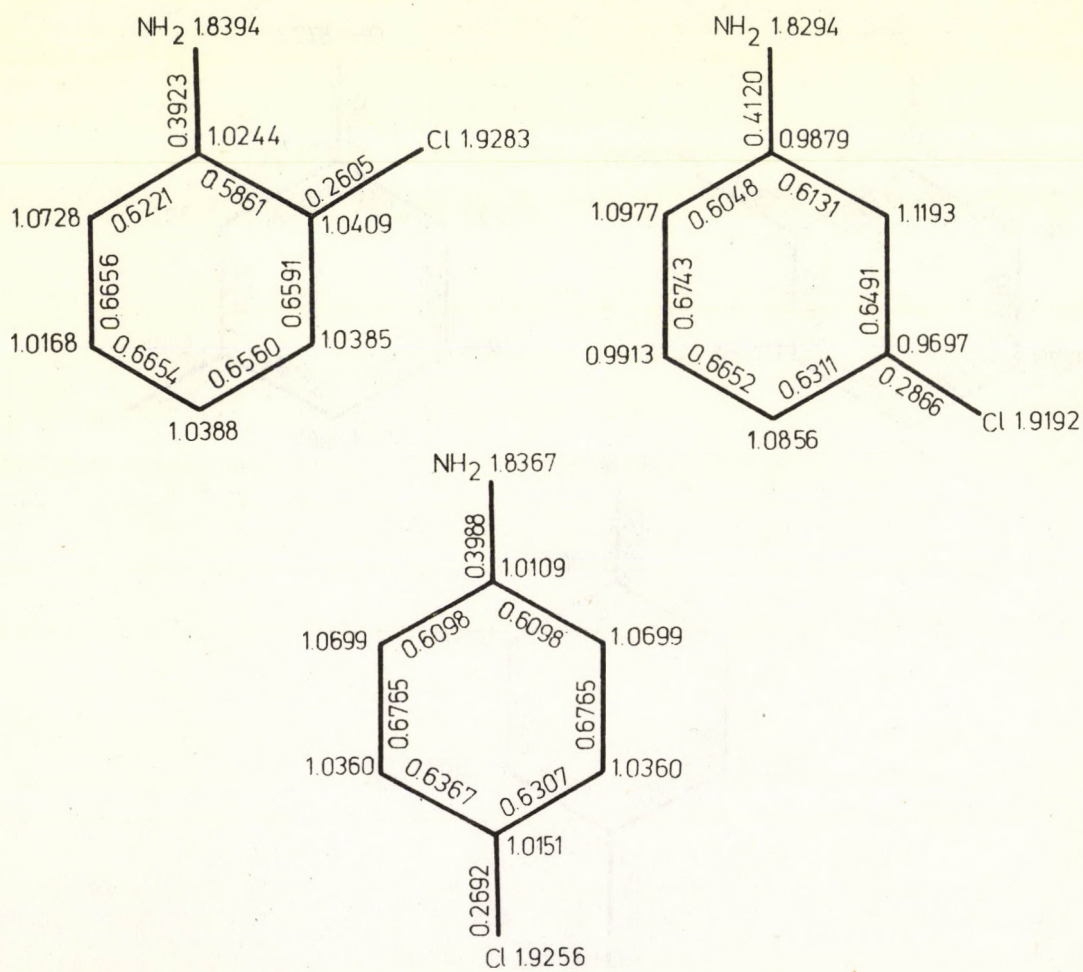
4.6 Dichloro Derivatives



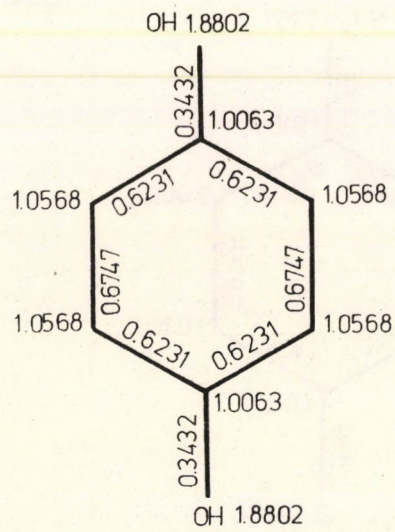
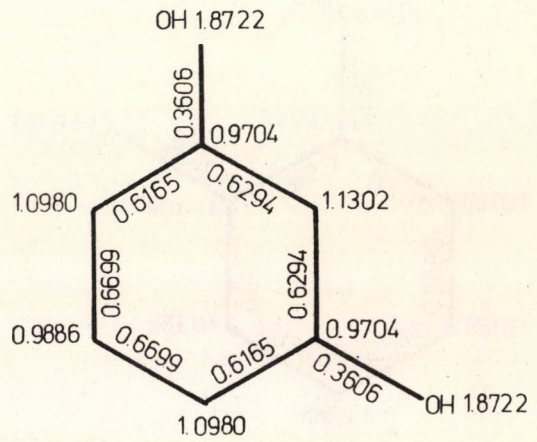
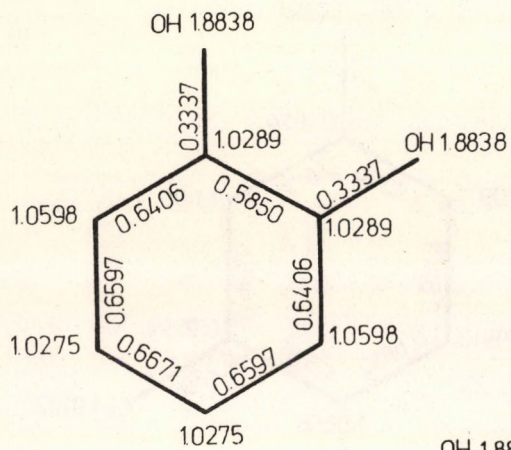
4.7 Hydroxy-chloro Derivatives



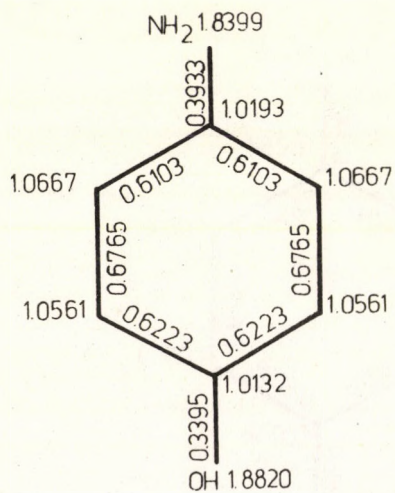
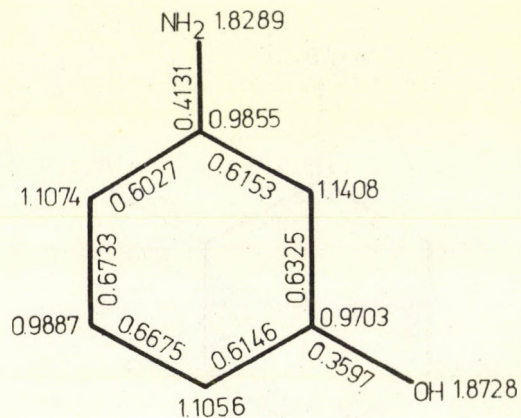
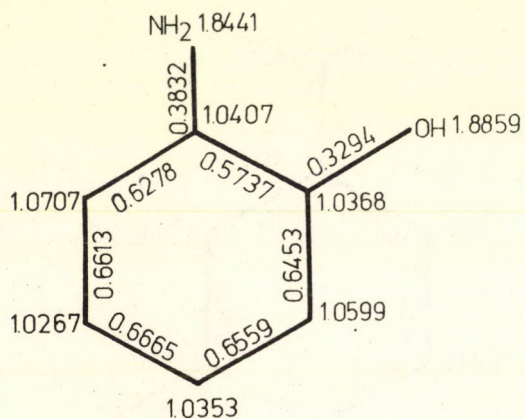
4.8 Amino-chloro Derivatives



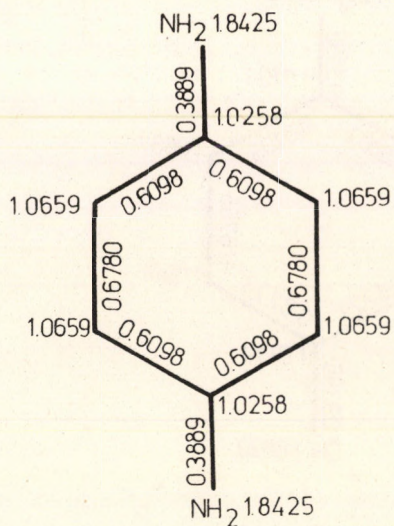
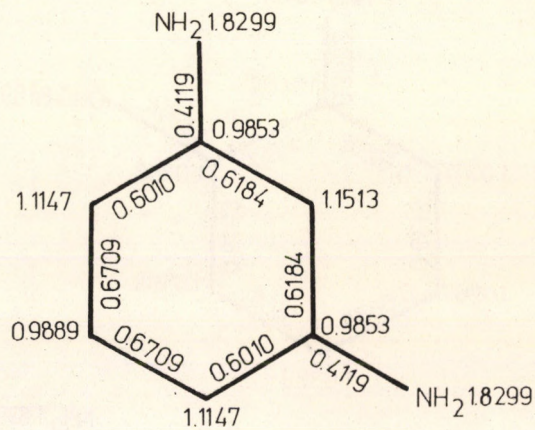
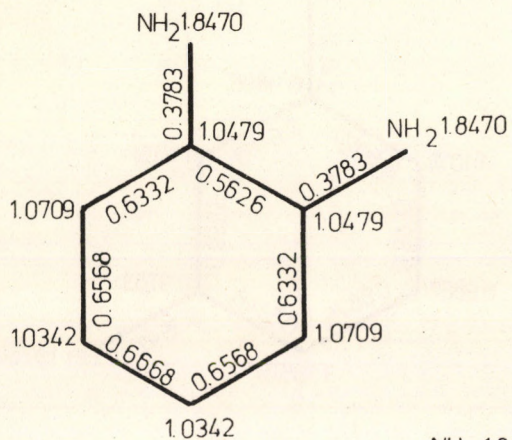
4.9 Dihydroxy Derivatives

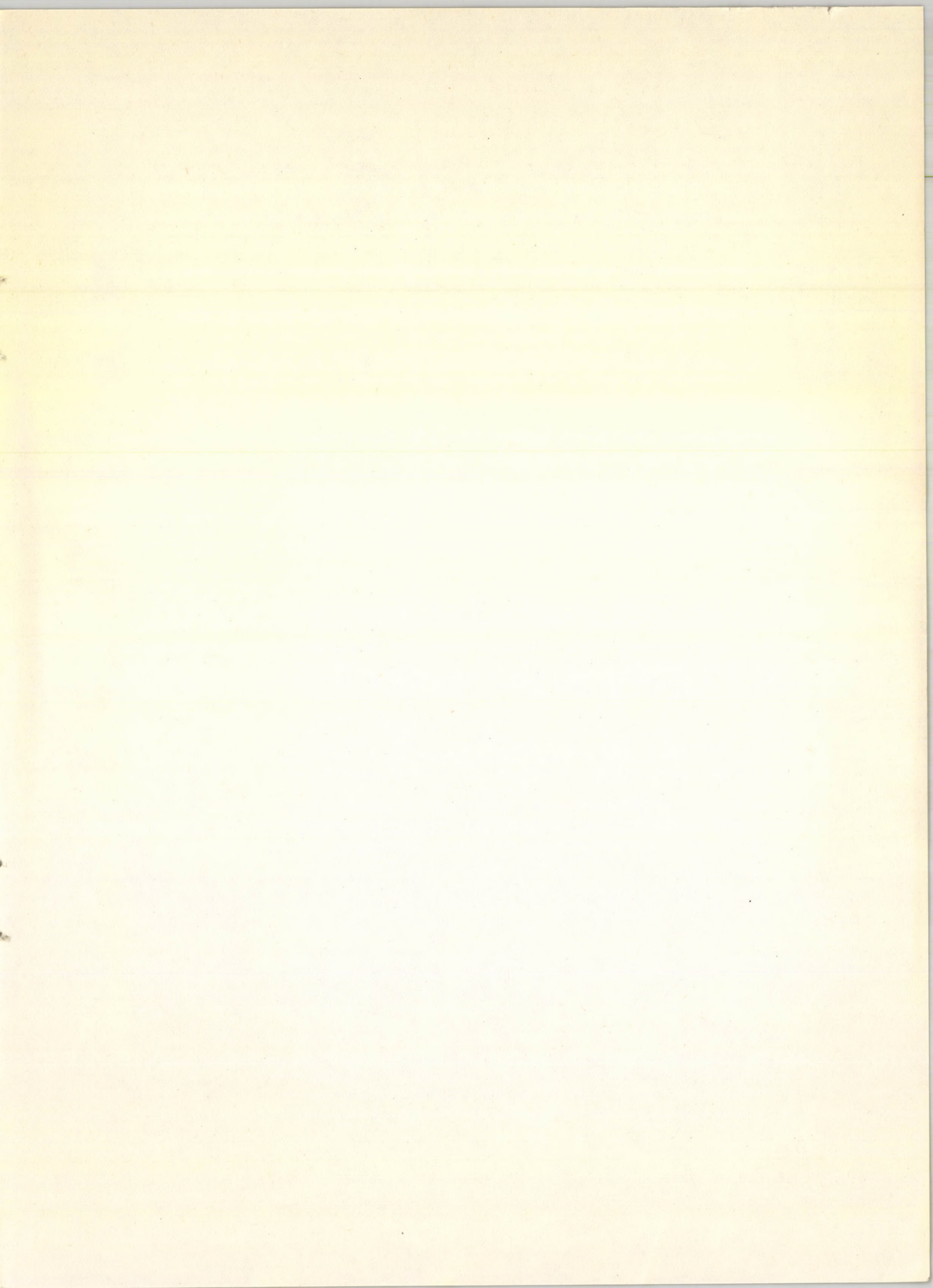


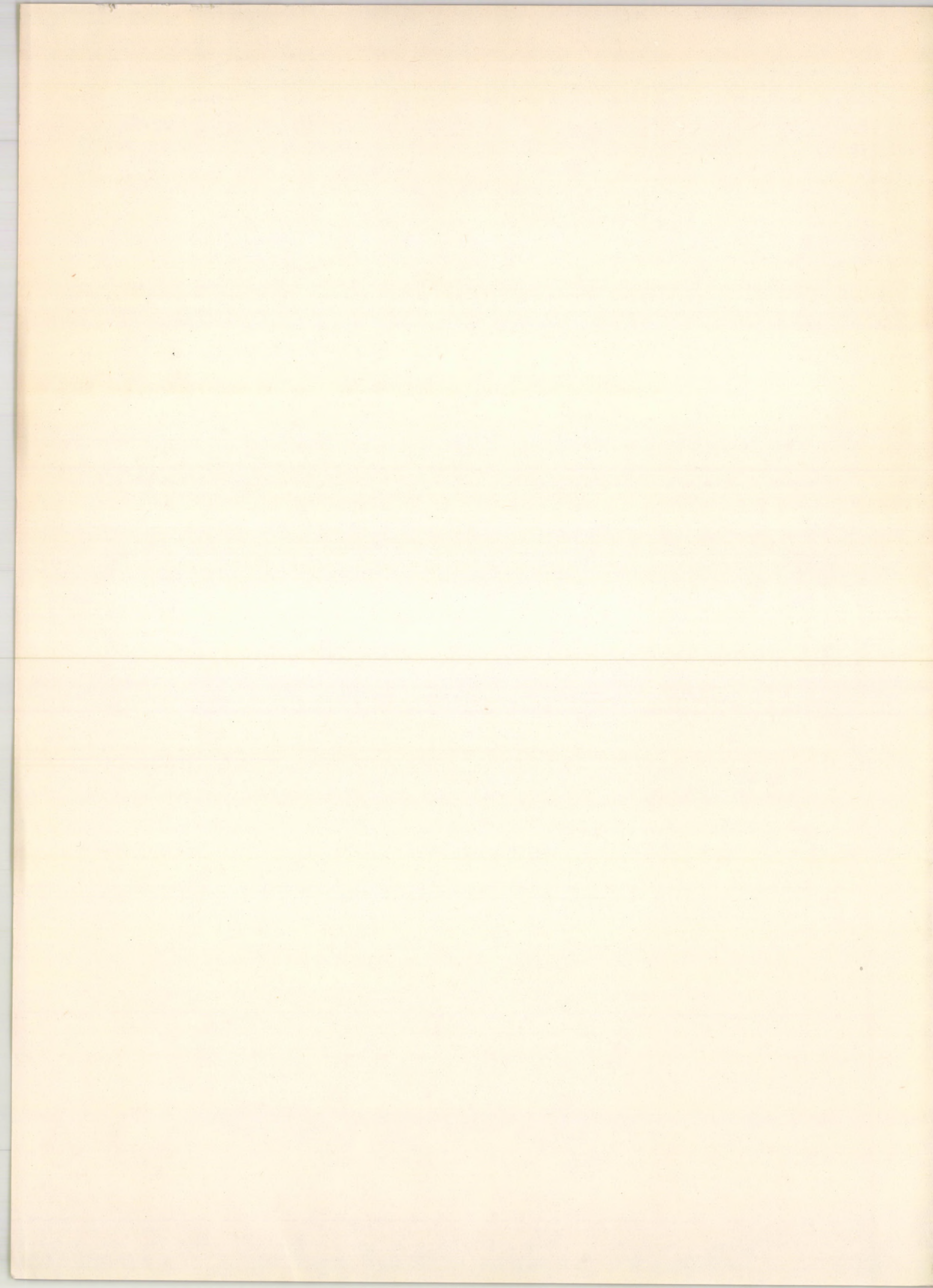
4.10 Hydroxy-Amino Derivatives

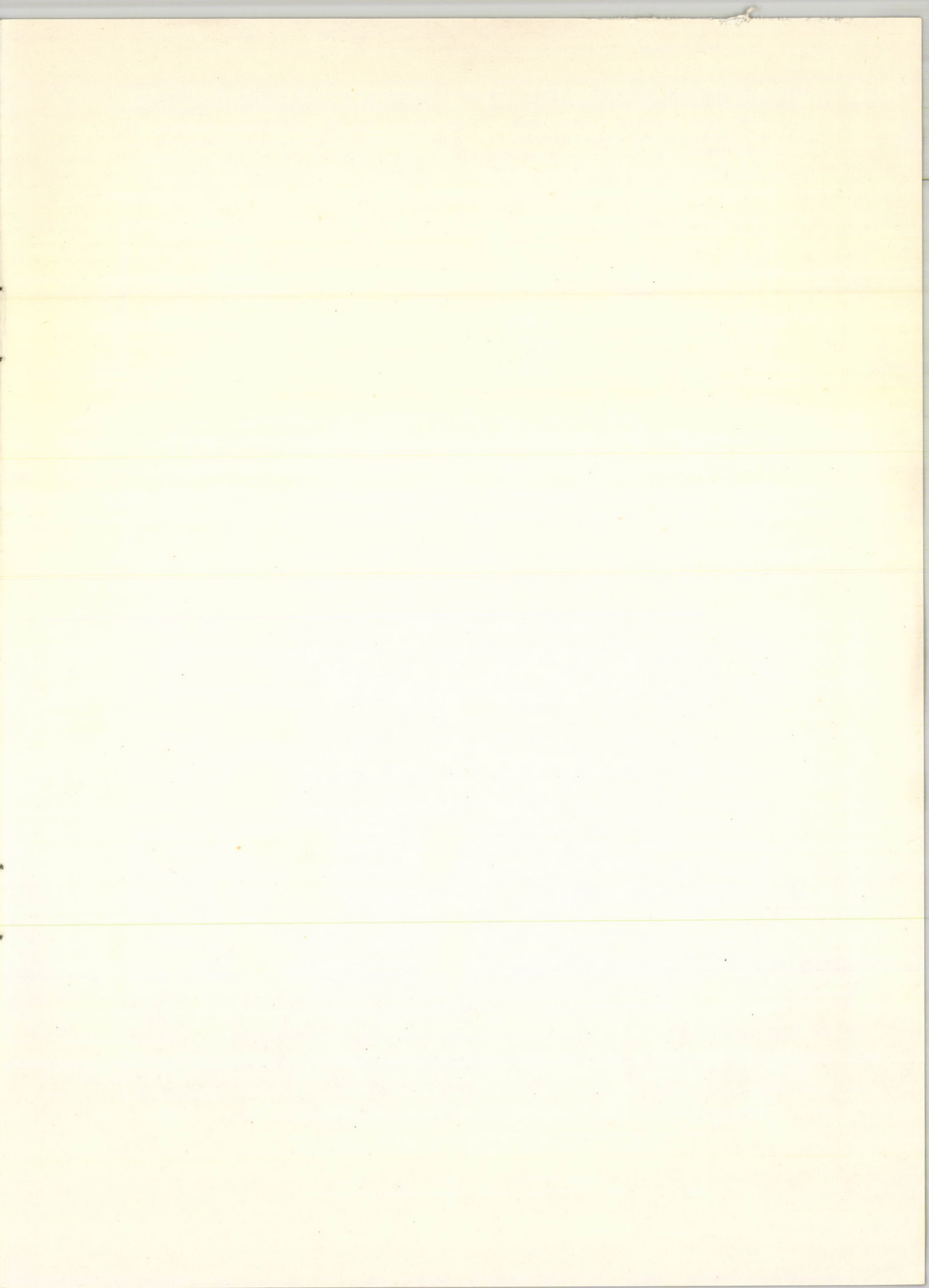


4.11 Diamino Derivatives









61.982



Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Kroó Norbert, a KFKI
Fizikai-Optikai Tudományos Tanácsának elnöke
Szakmai lektor: Kapuy Ede
Nyelvi lektor: T. Wilkinson
Példányszám: 200 Törzsszám: 72-7351
Készült a KFKI sokszorosító üzemében
Budapest, 1972. október hó