cadmium acetate are placed in an autoclave, and acetylene is delivered. The rotating autoclave is heated for 4 h at 180°C. The autoclave is cooled, the reaction mixture unloaded and redistilled under vacuum. Yield 2.9 g (40%) of the ether II, bp 70-72°C (2 hPa); n_D^{20} 1.4700; d_4^{20} 1.1250. Found: C 52.6; H 5.6; N 15.0%; M 186.8; MR_D 45.13. $C_8H_{10}N_2O_3$. Calculated: C 52.7; H 5.51 N 15.4%; M 182; MR_D 46.27.

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INTERACTION OF N,N'-POLYOXYETHYLENEDIPHTHALIMIDES WITH DIETHYLENETRIAMINE AND MASS SPECTRAL BEHAVIOR OF THE MACROCYCLIC DIAMIDES OF PHTHALIC ACID FORMED

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The reaction of diethylenetriamine and diphthalimides containing a polyoxyethylene fragment yielded macrocyclic diamides of phthalic acid, and the fragmentation of these compounds under the action of electron impact was studied. It was established that their decomposition consists of an initial ejection of a C_2H_4N radical, presuming a rearrangement of the molecular ions to the corresponding N-substituted phthalimides, followed by the splitting out of ethylene oxide and water molecules in various orders. These mass spectral principles can be used to establish the number and sequence of monomer units in the macrocycles.

It is known that the reaction of N,N'-polyoxyethylenediphthalimides with polyoxyethylenediamines leads to macrocyclic diamides of phthalic acid [1, 2]. However, the necessity of the conversion of part of the polyoxyethylenediphthalimide to polyoxyethylenediamine [3] and the use of the latter in the synthesis of macrocyclic diamides is a shortcoming of this method.

We found that macrocyclic diamides of phthalic acid IIb-d are formed in the action of readily available diethylenetriamine on the diphthalimides Ib-d in methanol—water medium.

A small amount of 3-azapentane-1,5-diphthalimide (III) is formed as a side product of the reaction, and its presence hinders the isolation of the compound IIa in pure form.

A convenient analytical method for establishing the structure of the products of the reaction described is the method of mass spectrometry.

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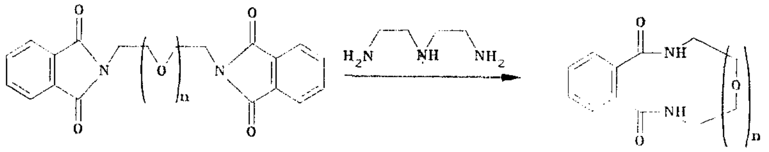


Ia d

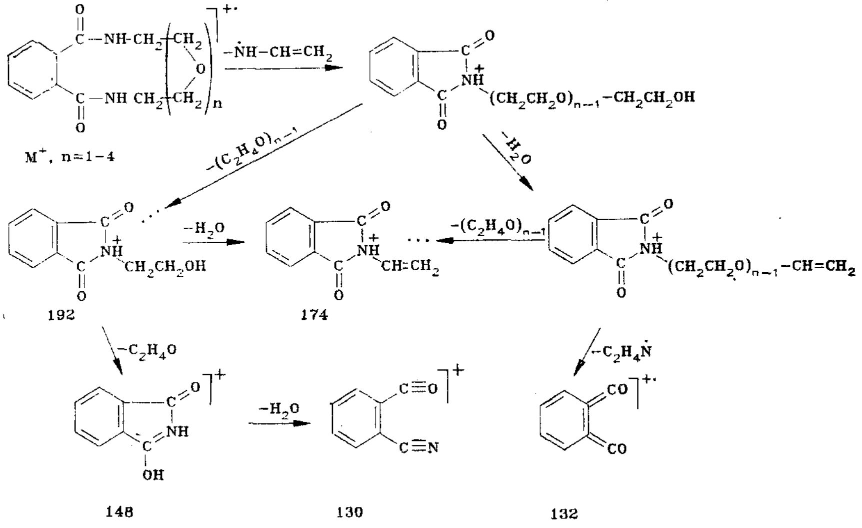
IIa-d

I,IIa n=1; b n=2; c n=3; d n=4

In the mass spectra of compounds IIa-d (Table 1) there are peaks of molecular ions (M^+) with m/z 234 (IIa)*, 278 (IIb), 322 (IIc), and 366 (IId). The most characteristic pathway of decomposition of M^+ of compounds IIa-d is associated with the formation of the ion $[M - C_2H_4N]^+$ and the series of ions $[M - C_2H_5N, -n\text{-}C_2H_4O]^+$, where n = 1(IIa); 1, 2 (IIb); 1, 2, 3 (IIc) and 1, 2, 3, 4 (IId). These ions, in turn, may break down, eliminating a water molecule and forming a series of homologous ions $[M - C_2H_4N, -H_2O\ -n\text{-}C_2H_4O]^+$ where n = 0-4. The series of peaks corresponding to these homologous ions are readily followed in the mass spectrum of compound IId. The elementary compositions of the ions under consideration are cited below: M^+, 366, $C_{18}H_{26}O_6N_2$; $[M - C_2H_4N]^+$, 324, $C_{16}H_{22}O_6N$; $[M - C_2H_4N, - H_2O]^+$, 306, $C_{16}H_{20}O_5N$; $[M - C_2H_4N, -C_2H_4O]^+$, 280, $C_{14}H_{18}O_5N$; $[M - C_2H_4N, -H_2O, -C_2H_4O]^+$, 262, $C_{14}H_{16}O_4N$; $[M - C_2H_4N, -2C_2H_4O]^+$, 236, $C_{12}H_{14}O_4N$; $[M - C_2H_4N, -H_2O, -2C_2H_4O]^+$, 218, $C_{12}H_{12}O_3N$; $[M - C_2H_4N, -3C_2N_4O]^+$, 192, $C_{10}H_{10}O_3N$; $[M - C_2H_4N, -H_2O, -3C_2H_4O]^+$, 174, $C_{10}H_8O_2N$; $[M - C_2H_4N, -4C_2H_4O]^+$, 148, $C_8H_6O_2N$; $[M - C_2H_4N, -H_2O, -3C_2H_4O_2, -C_2H_4N]^+$, 132, $C_8H_4O_2$; $[M - C_2H_4N, -H_2O, -4C_2H_4O]^+$, 130, $C_8H_4ON^+$.

The data of elementary analysis of the ions show that the decomposition of M^+ of IIa-d proceeds by successive cleavage of CO—NH bonds, one of the CH_2—O or N—CH_2 bonds, with migration of a hydrogen atom from the fragment being eliminated to an oxygen or nitrogen atoms of the charged fragment.

Considering the tendency of amides of phthalic acid for cyclization in thermolysis and electron impact, forming the corresponding phthalimides [2], and on the basis of data on the fragmentation of N-substituted phthalimides [4], as well as the data of the mass spectra of the diphthalimides Ia-d (Table 1), for which, after elimination from M^+ of the fragments $C_6H_4(CO)_2NH$ (compounds Ia, b) or $C_6H_4(CO)_2N{=}CH_2$ (compounds Ib, c), followed by elimination of fragments of the polyoxyethylene chain, the formation of the ions 174 $[C_6H_4(CO)_2NHCH{=}CH_2]^+$, 160 $[C_6H_4(CO)_2N{=}CH_2]^+$ and 148 $[C_6H_4(CO)_2NH_2]^+$, analogous to the ions observed in the spectra of compounds IIa-d, is characteristic, it can be assumed that the ion detected as a result of such decomposition most likely has the structure of an N-substituted phthalimide:



The presence of the peak of M^+ and the peaks of the ions $[M - C_2H_4N, -n\text{-}C_2H_4O]_6$ and $[(M - C_2H_4N, -n\text{-}C_2H_4O) - H_2O]^+$ in the mass spectra of macrocyclic diamides of phthalic acid permits the establishment both of the molecular weight of the investigated compound and of the sequence of monomer units in the macrocycle.

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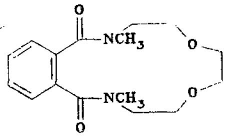
*Here and henceforth in the text and schemes, the numbers characterizing the ions define the value of m/z.

TABLE 1. Mass Spectra of Compounds Ia-d, IIa-d, and IV

Compound	Values of m/z, (intensity of peak in % of maximum)
Ia	365 (3), 364 (2), 217 (60), 204 (29), 190 (16), 174 (100), 173 (94), 160 (96), 148 (8), 147 (67), 146 (17), 133 (22), 132 (10), 131 (9), 130 (78), 129 (20)
Ib	409 (1), 408 (1), 261 (7), 234 (14), 218 (20), 217 (16), 204 (14), 190 (5), 174 (100), 173 (90), 160 (86), 148 (21), 147 (33), 146 (15), 133 (41), 132 (18), 131 (16), 130 (72), 129 (45)
Ic	452 (0,2), 292 (2), 278 (6), 262 (3), 261 (3), 239 (2), 218 (15), 204 (9), 192 (4), 191 (3), 174 (100), 160 (35), 148 (8), 147 (28), 146 (5), 133 (12), 132 (4), 131 (8), 130 (43), 129 (15)
Id	496 (0,5), 336 (1), 322 (2), 305 (3), 262 (6), 218 (28), 204 (11), 192 (1), 190 (2), 174 (100), 160 (37), 148 (11), 147 (35), 146 (8), 133 (14), 132 (8), 131 (16), 130 (48), 129 (23)
IIa	235 (1,3), 234 (2,4), 233 (5,8), 217 (21), 205 (43), 192 (20), 190 (12), 175 (99), 174 (62), 161 (20), 160 (49), 148 (44), 147 (100), 146 (8), 133 (11), 132 (23), 131 (5), 130 (38), 129 (5)
IIb	279 (4,7), 278 (2,7), 277 (3), 261 (5), 236 (29), 218 (17), 205 (7), 192 (19), 190 (46), 174 (84), 161 (100), 160 (37), 148 (97), 147 (29), 133 (19), 132 (47), 131 (16), 130 (50), 129 (8)
IIc	324 (1,5), 323 (8), 322 (2), 321 (3,5), 305 (3), 280 (55), 262 (4), 236 (21), 218 (9), 205 (37), 192 (16), 190 (38), 174 (100), 161 (50), 160 (31), 148 (92), 147 (57), 133 (14), 132 (22), 131 (8), 130 (5), 129 (8)
IId	368 (1,2), 367 (4,1), 366 (1,9), 365 (2,5), 349 (1), 324 (28), 306 (2), 280 (15), 262 (2), 236 (11), 218 (11), 205 (5), 192 (14), 190 (21), 174 (100), 161 (52), 160 (19), 149 (53), 148 (41), 147 (26), 133 (11), 132 (17), 131 (6), 130 (36), 129 (6)
IV	306 (42), 278 (9), 263 (6), 262 (6), 250 (24), 235 (33), 232 (10), 218 (4), 206 (38), 188 (30), 175 (96), 162 (100), 148 (9), 147 (25), 146 (35), 145 (30), 144 (20), 133 (65), 132 (75), 131 (20), 130 (30)

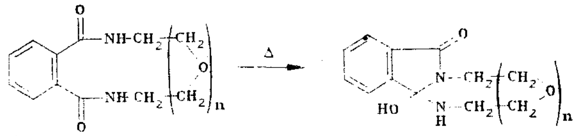
To confirm the proposed mechanism of fragmentation we investigated the mass spectrometric behavior of the diamide of phthalic acid IV, which differs from compound IIb in that the hydrogen atoms of the nitrogen atoms are replaced by methyl groups in it. The presence of N-methyl groups in compound IV leads to the fact that in the first act of fragmentation, the $H_3C{-}N{-}CH{=}CH_2$ group is eliminated from M^+ (Table 1). The spectrum contains a series of homologous ions $[M - CH_3C_2H_3N, n\text{-}C_2H_4O]^+$ and $[M - CH_3C_2H_3N, -n\text{-}C_2H_4O - H_2O]^+$, where n = 0-2. The elementary composition of these ions is cited below: M^+, 306, $C_{16}H_{22}O_4N_2$; $[M - CH_3C_2H_3N]^+$, 250, $C_{13}H_{16}O_4N$; $[M - CH_3C_2H_3N, -C_2H_4O]^+$, 206, $C_{11}H_{12}O_3N$; $[M - CH_3C_2H_3N, -2C_2H_4O]^+$, 162, $C_9H_8O_2N$. Further decomposition of the N-methylphthalimide ion, 162, agrees with the known data [4].

A characteristic peculiarity of the mass spectrum of compound IV is the absence of a peak of the ion $[M - OH]^+$, observed in the spectra of the compounds IIa-d.



IV

This fact supports the participation of the amide hydrogen atom in the formation of the $[M - OH]^+$ ion. Considering the data of [5], we can assume that the formation of this ion is preceded by rearrangement of compounds IIa-d with the formation of cyclic analogs of phthalimides:



The breakdown of these polycyclic compounds in electron impact is associated with elimination of the hydroxy group and decomposition of the macrocyclic system. We should mention that this type of fragmentation is not essential in the spectra of compounds IIa-d and has no serious analytical application, in contrast to the first type of decomposition, which begins with the formation of the ion $[M - C_2H_4N]^+$.

It is also interesting that the presence of methyl substituents at the nitrogen atom in compound IV substantially changes the nature of the decomposition of its M^+. Intense peaks of the ions $[M - CO]^+$, 278, $C_{15}H_{22}O_3N_2$ and $[M - CO, -C_2H_5N]^+$, 235, $C_{13}H_{17}O_3N$ appear in the spectrum but are absent in the mass spectrum of its analog IIb.

Thus, our investigation of the peculiarities of the mass spectrometric behavior of macrocyclic diamides of phthalic acid shows that M^+ of compounds IIa-d, analogously to the behavior of the substances themselves in thermolysis, are readily rearranged forming the corresponding ions of N-substituted phthalimides.

EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer 580B spectrophotometer in tablets with potassium bromide. The mass spectra were obtained on a LKB-9000 instrument at an ionizing voltage of 70 eV with direct introduction of the sample into the source; the temperature of evaporation of the sample was 40-100°C, temperature of the ionization chamber 220°C. The precise values of the masses of the ions were measured on a Varian CH-5 instrument with a resolving power R = 10,000 and energy of ionizing electrons 70 eV. Thin-layer chromatography was conducted on Silufol UV-254 plates, elution with acetone, and development in UV light and with ninhydrin.

N,N'-Substituted diphthalimides Ia-d were produced according to the procedure of [3], compound IV according to [6], and the diamide IIa according to [1].

Macrocyclic Diamides of Phthalic Acid IIb-d. A mixture of 10 mmoles of the diphthalimide Ib-d, 15 mmoles diethylenetriamine, 15 ml of water, and 300 ml of methanol was mixed at room temperature for 7 days. The products IIb-d formed were isolated by column chromatography on silica gel and eluted with acetone. Yield of II, %: 35 (n = 2); 5 (n = 3); 6 (n = 4). The constants and IR spectral characteristics of the compounds obtained were identical with those described in [1, 2]. In the production of compound IIb, 0.07 g of 3-azapentane-1,5-diphthalimide was isolated; its constants corresponded to those cited in [7].

When 0.3 g of the diamide IIc was heated for 20 min at 250°C under vacuum, followed by isolation by column chromatography, 0.1 g of the diphthalimide Ic was formed, the constants of which corresponded to those cited in [3].

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