1,2-DIISOPHTHALIMIDOETHANE. X-RAY DIFFRACTION EVIDENCE FOR THE STRUCTURE OF THE PRODUCT OF ACYLATION OF 1,2-DIAMINOETHANE WITH PHTHALOYL CHLORIDE

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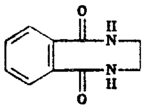
It was demonstrated by x-ray diffraction investigation of the product of the reaction of 1,2-diaminoethane with phthalic acid dichloride that the resulting compound has the 1,2-diisophthalimidoethane structure. An improved method for its synthesis is proposed.

The preparation of phthalic acid cyclic diamide I by the reaction of phthaloyl chloride with 1,2-diaminoethane has been reported [1]. Wolfe and Hasan [2] later repeated the research reported in [1] and proposed bicyclic imide structures II for the compound under consideration. On the basis of a comparison of the chemical properties and IR and mass-spectral characteristics of the compounds under discussion with the properties of isophthalimides [3], isoimide structure III was proposed for it in [4].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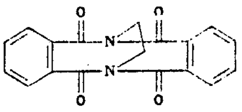
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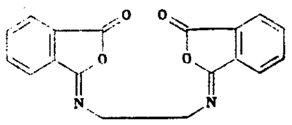
III

To unequivocally solve the problem of the structure of the product of acylation of 1,2-diaminoethane with phthaloyl chloride we used x-ray diffraction analysis to determine the molecular and crystal structure of the compound formed in accordance with the methods in [1, 2]. The identical character of the investigated sample and the compound described in [1, 2] was established on the basis of the identical character of the constants and the IR spectra (the complete IR spectrum is presented in [2]).

The presence in the unit cell of the investigated crystal of two formula units with the composition $C_{18}H_{12}N_2O_4$ makes it possible to assert that the compound belongs to the structural class $P2_1/n$, $Z = 2(\bar{1})$ [*] [5]. This immediately rejects structure I and suggests that half of the molecule is an independent part, i.e., it indicates the possibility of structure II or III, since the two imide fragments in the molecule are situated symmetrically and at a maximum distance from one another. We used x-ray diffraction analysis to establish a three-dimensional model of 1,2-diisophthalimidoethane III, which is presented, along with the designations, in Fig. 1. The coordinates of the atoms, the lengths of the bonds between them, and the bond angles are presented in Tables 1-3. The length of the $C_{(9)}-C^{*}_{(9)}$ bond, relative to which the nitrogen atoms exist in a hindered conformation, is 1.512 Å and is characteristic for a $C_{sp^3}-C_{sp^3}$ single bond. The $C_{(9)}-N$ bond is equal to 1.465 Å and has pronounced single-bond character. Each isophthalimide fragment of III is virtually planar – the dihedral angle between the planes of the phenyl and isoimide rings is 0.3°. The deviations of the N and $O_{(2)}$ atoms from the rms of the plane of the isophthalimide fragment are –0.048 and 0.010 Å, respectively. The distances between the carbon atoms in the six-membered ring averaged out to 1.383 Å and are the usual values for aromatic systems. The distribution of the angles is also characteristic for such compounds. Thus, the endocyclic angles at the $C_{(1)}$ and $C_{(4)}$ atoms are shortened to 117° (Table 3); this was previously observed for phthalimides with normal structures [6-8] and N-phenylphthalimidine [8]. In the five-membered iso-

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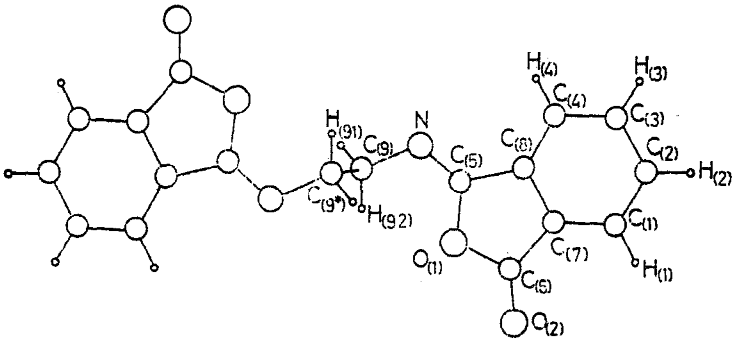

Fig. 1. Three-dimensional structure of III.

TABLE 1. Coordinates of the Basis Atoms with Standard Deviations $\cdot 10^4$ ($\cdot 10^3$ for the H atoms) in the Structure of III

Atom*	*x*	*y*	*z*	Atom*	*x*	*y*	*z*
$O_{(1)}$	3522(1)	3716(1)	1546(2)	$C_{(7)}$	935(2)	3407(1)	−391(3)
$O_{(2)}$	3476(2)	2900(1)	−1664(2)	$C_{(8)}$	720(2)	3907(1)	1523(3)
N	2728(2)	4524(1)	4618(2)	$C_{(9)}$	4475(2)	4632(1)	5566(3)
$C_{(1)}$	−390(2)	3106(1)	−1935(3)	$H_{(1)}$	−19(2)	278(1)	−323(3)
$C_{(2)}$	−1339(3)	3331(1)	−1491(4)	$H_{(2)}$	−289(3)	312(1)	−251(3)
$C_{(3)}$	−2150(2)	3837(1)	423(4)	$H_{(3)}$	−325(3)	397(1)	67(3)
$C_{(4)}$	−829(2)	4135(1)	1965(3)	$H_{(4)}$	−97(2)	450(1)	318(3)
$C_{(5)}$	2357(2)	4100(1)	2790(3)	$H_{(91)}$	443(2)	472(1)	731(3)
$C_{(6)}$	2700(2)	3277(1)	−373(3)	$H_{(92)}$	502(2)	418(1)	528(3)

*The numbering of the atoms is presented in Fig. 1.

phthalimide ring, the geometrical characteristics of which have not been previously described, let us note the delocalization of the electron density in the acceptor O═C—O—C═N chain. The $C_{(5)}$—$O_{(1)}$ distance is 1.403 Å and the $C_{(6)}$—$O_{(1)}$ distance is 1.392 Å; these distances are shortened and have the same sesqui character as in heteroanalogs of III — imides and imidines [8]. The $C_{(6)}$—$O_{(2)}$ and $C_{(5)}$—N distances, which are, respectively, 1.198 and 1.258 Å, have pronounced double-bond character. The $C_{(5)}$—$C_{(8)}$ and $C_{(6)}$—$C_{(7)}$ distances are only slightly shortened as compared with single C—C bonds and are close to the values found in [8]. The intramolecular steric hindrance in III leads to a substantial difference in the exocyclic bond angles at the $C_{(6)}$ atoms: $O_{(2)}$—$C_{(6)}$—$C_{(7)}$ = 132.5°, and $O_{(2)}$—$C_{(6)}$—$O_{(1)}$ = 119.8°. This is also true for the angles at the $C_{(5)}$ atom: N—$C_{(5)}$—$C_{(8)}$ = 129.0°, and N—$C_{(5)}$—$O_{(1)}$ = 123.6° (Table 3). This difference is a consequence of the electrostatic interaction of the protons attached to the $C_{(1)}$ and $C_{(4)}$ atoms with the $O_{(2)}$ and N atoms. The average C_{sp^3}—H distance is 0.95 Å, and the average C_{sp^3}—H distance is 0.98 Å. Angles at the C atom of the CCH type average 120° in an aromatic system, and the angles at the $C_{(9)}$ atom are close to the tetrahedral values.

In contrast to the packing of phthalimides with normal structures, for which intermolecular contacts are realized between the imide and aromatic rings [8], for the packing of molecules of III in the crystal an intermolecular dipole—dipole interaction $C_{(6)}$—$O_{(2)}$...$C^*_{(6)}$—$O^*_{(2)}$ = 2.89 Å between the molecules linked by a double-helical axis parallel to the Z axis is characteristic. Taking this into account, one can assert that the crystal structure is lamellar; the layers are directed parallel to the (110) plane, and a van der Waals interaction is realized between them.

Thus, as a result of our x-ray diffraction study, we have unequivocally confirmed the structure of the product of the reaction of 1,2-diaminoethane with phthaloyl chloride as 1,2-diisophthalimidoethane III and thereby have established for the first time the molecular structure of the isophthalimide system. The isophthalimide fragments in the molecule exist in a hindered conformation relative to the $C_{(9)}$—$C^*_{(9)}$ bond. On the basis of data on the isoimide structure of III and the conditions of the formation of isophthalimides in the reaction of phthaloyl chloride with primary amines [9] we have obtained 1,2-diisophthalimidoethane in higher yield than in the case of the known methods [2, 4].

TABLE 2. Bond Lengths d (Å) in III (standard deviations given in parentheses)

Bond	d	Bond	d
$C_{(1)}-C_{(2)}$	1,377(3)	$O_{(1)}-C_{(6)}$	1,392(2)
$C_{(1)}-C_{(7)}$	1,386(2)	$O_{(2)}-C_{(6)}$	1,198(2)
$C_{(2)}-C_{(3)}$	1,389(3)	$N-C_{(5)}$	1,258(2)
$C_{(3)}-C_{(4)}$	1,381(2)	$N-C_{(9)}$	1,465(2)
$C_{(4)}-C_{(8)}$	1,379(2)	$C_{(1)}-H_{(1)}$	0,93(2)
$C_{(8)}-C_{(7)}$	1,383(2)	$C_{(2)}-H_{(2)}$	0,96(2)
$C_{(5)}-C_{(8)}$	1,469(2)	$C_{(3)}-H_{(3)}$	0,96(2)
$C_{(6)}-C_{(7)}$	1,463(2)	$C_{(4)}-H_{(4)}$	0,93(2)
$C_{(9)}-C^{*}_{(9)}$	1,512(3)	$C_{(9)}-H_{(91)}$	0,98(2)
$O_{(1)}-C_{(5)}$	1,403(2)	$C_{(9)}-H_{(92)}$	0,97(2)

TABLE 3. Bond Angles (deg) in the Structure of III (standard deviations given in parentheses)

Angle	Value	Angle	Value
$C_{(7)}-C_{(1)}-C_{(2)}$	117,0(2)	$O_{(2)}-C_{(6)}-C_{(7)}$	132,5(1)
$C_{(1)}-C_{(2)}-C_{(3)}$	121,1(2)	$N-C_{(5)}-C_{(8)}$	129,0(1)
$C_{(2)}-C_{(3)}-C_{(4)}$	121,9(2)	$N-C_{(5)}-O_{(1)}$	123,6(1)
$C_{(3)}-C_{(4)}-C_{(8)}$	117,0(2)	$C_{(7)}-C_{(1)}-H_{(1)}$	119(1)
$C_{(1)}-C_{(7)}-C_{(8)}$	121,9(1)	$C_{(2)}-C_{(1)}-H_{(1)}$	124(1)
$C_{(4)}-C_{(8)}-C_{(7)}$	121,2(1)	$C_{(1)}-C_{(2)}-H_{(2)}$	119(1)
$C_{(1)}-C_{(7)}-C_{(6)}$	130,0(1)	$C_{(3)}-C_{(2)}-H_{(2)}$	120(1)
$C_{(4)}-C_{(8)}-C_{(5)}$	131,3(1)	$C_{(4)}-C_{(3)}-H_{(3)}$	120(1)
$C_{(5)}-N-C_{(9)}$	118,7(1)	$C_{(2)}-C_{(3)}-H_{(3)}$	118(1)
$N-C_{(9)}-C^{*}_{(9)}$	110,0(2)	$C_{(8)}-C_{(4)}-H_{(4)}$	122(1)
$C_{(5)}-C_{(8)}-C_{(7)}$	107,5(1)	$C_{(3)}-C_{(4)}-H_{(4)}$	121(1)
$C_{(6)}-C_{(7)}-C_{(8)}$	108,1(1)	$C^{*}_{(9)}-C_{(9)}-H_{(91)}$	108(1)
$C_{(8)}-C_{(5)}-O_{(1)}$	107,4(1)	$C^{*}_{(9)}-C_{(9)}-H_{(92)}$	109(1)
$C_{(5)}-O_{(1)}-C_{(6)}$	109,3(1)	$N-C_{(9)}-H_{(91)}$	108(1)
$O_{(1)}-C_{(6)}-C_{(7)}$	107,6(1)	$N-C_{(9)}-H_{(92)}$	113(1)
$O_{(2)}-C_{(6)}-O_{(1)}$	119,8(1)	$H_{(91)}-C_{(9)}-H_{(92)}$	108(1)

EXPERIMENTAL

The IR spectra of KBr pellets were recorded with a Perkin–Elmer 580 B spectrometer. The mass spectra were obtained with a Varian MAT-112 spectrometer; the ionizing voltage was 70 eV, and the samples were introduced directly into the source. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates with elution with acetone–hexane (1:2) and development in UV light and by ninhydrin (blue spots).

For the x-ray diffraction analysis we selected single crystals with a prismatic habitus with linear dimensions 0.30 × 0.35 × 0.15 mm. The crystal was monoclinic with the following unit cell parameters: a = 7.985(1), b = 16.924(3), c = 5.520(1) Å, γ = 99.88(2)°, V = 735(1) Å^3, symmetry space group $P2_1/n$, Z = 2, $C_{18}H_{12}N_2O_4$, and d_{calc} 1.447 g/cm^3. The experimental data were obtained with an NIKOLET R-3 diffractometer in Mo K_α emission; $2\theta_{max}$ = 60°. A total of 837 reflections, 825 of which with $I \geq 3\sigma(I)$ were used to determine and refine the structure, was recorded. The structure was solved by the direct method within the framework of the SHELXTL complex [10] and was refined within the anisotropic approximation for the C, O, and N atoms and within the isotropic approximation for the H atoms. The latter were found objectively from differential Fourier syntheses. The final R factor was 0.026.

1,2-Diisophthalimidoethane III. A) Compound III was obtained as described in [2] by the simultaneous dropwise addition of solutions of 2.0 g (0.01 mole) of phthaloyl chloride in 200 ml of absolute benzene and 1.2 g (0.02 mole) of anhydrous 1,2-diaminoethane in 200 ml of benzene to 150 ml of stirred absolute benzene with subsequent filtration of the reaction mixture and crystallization and recrystallization of the desired product from benzene. The yield was 0.1 g (6%). The colorless crystals had mp 224-227°C and R_f 0.29. IR spectrum: 1785 (C=O); 1709 (C=N); 1260, 925 cm^{-1} (C–O–C). Mass spectrum, m/z ($I \geq 10\%$): 76 (40), 77 (37), 104 (29), 105 (14), 129 (15), 132 (18), 160 (100), 161 (31), 172 (12), 320 (3, M$^+$). According to the data in [2], the yield was 0.319 g (20%), and the product had mp 224-227°C; IR spectrum: 1785 (C=O), 1709 cm^{-1} (C=N); M$^+$ 320.0797.

B) A solution of 4.1 g (0.02 mole) of phthaloyl chloride in 200 ml of absolute dioxane solution containing 0.6 g (0.01 mole) of anhydrous 1,2-diaminoethane and 6.1 g (0.06 mole) of triethylamine, after which the mixture was maintained for 3 min and then filtered. The filtrate was concentrated in vacuo (60-80 mm Hg) to a volume of 10 ml, and the precipitated crystals were removed by filtration and recrystallized from acetone. The yield was 1.7 g (53%). The constants were identical to those presented above.

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REACTIONS OF 4-METHYL-7-DIETHYLAMINOCOUMARIN WITH ELECTROPHILIC REAGENTS

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The reactions of 4-methyl-7-diethylaminocoumarin with various electrophilic reagents — acetic anhydride, complexes of unsaturated compounds (styrene, dihydropyran, phenylacetylene) with Lewis acids, and copper halides — were used to synthesize 3-, 6-, and 8-substituted coumarins. It was shown that the selectivity of reactions involving substitution in the 3 position increases with an increase in the "softness" of the Lewis acid.

The special interest in 7-aminocoumarins is due to their effective application as laser dyes [1]. Most of the publications dealing with 7-aminocoumarins are devoted to methods for their synthesis and physicochemical characteristics, whereas little study has been devoted to the chemistry of the indicated compounds [2]. We began a systematic investigation of the chemical properties of 7-aminocoumarins, and in the present paper we will discuss a number of electrophilic substitution reactions in the case of 4-methyl-7-diethylaminocoumarin (I) — a typical representative of this class.

Several electrophilic substitution reactions are known in the 7-aminocoumarin series [2], e.g., nitration [3], sulfonation [4], which, as a rule, proceed under severe conditions and nonselectively and give mixtures of products of 3-, 6-, and 8-substitution in high yields.

We attempted to realize a number of new reactions in the case of coumarin I under standard conditions. We tested acetic anhydride, acetyl chloride, benzyl chloride, and benzenediazonium chloride as electrophilic reagents. Dichloroethane, benzene, acetic anhydride,

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