STRUCTURE OF 4,4',6,6'-TETRANITRO-2,2'-DICARBOXYBIPHENYL DIMETHYL ESTER

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To study the effect of the structures of nitro-substituted o-carboxybiphenyls on the course and the results of transformations of the latter in polar aprotic solvents we studied the structures of a number of nitro-substituted 2-carboxy- and 2,2'-dicarboxybiphenyls [1]. It was shown that the formation of OH...O bonded associates of the dimeric or chain type occurs in the crystal phase in all cases. It was also established that the investigated acids form hydrogen-bonded molecular complexes with polar aprotic solvents [2]. An x-ray diffraction study of 4,4',6,6'-tetranitro-2,2'-dicarboxybiphenyl dimethyl ester (I) was carried out to obtain data on the structure of the molecule in the case of exclusion of the effect of intermolecular H bonds on the conformational and geometrical parameters of the biphenyl system. The synthesis of ester I was accomplished by esterification of 4,4',6,6'-tetranitro-2,2'-dicarboxybiphenyl (II) with methanol using catalytic amounts of sulfuric acid. The structure of the crystals of acid II was described in [3]. Nitro-substituted o-carboxybiphenyls and their esters, including I, have also been studied by means of IR spectroscopy [4].

The x-ray diffraction experiment was carried out with a Syntex  $P\bar{l}$  automatic diffractometer (Mo emission, Nb filter,  $6/2\theta$  scanning up to  $2\theta = 48^{\circ}$ ). The pale-yellow transparent crystals of I, obtained by recrystallization from acetic acid, were rhombic and had the fol-

Atom	x	y	z	Ueq iso
$\begin{array}{c} \text{Atom} \\ \hline \\ O(1) \\ O(2) \\ O(3) \\ O(5) \\ O(7) \\ O(6) \\ O(7) \\ O(8) \\ O(10) \\ O(10) \\ O(11) \\ O(12) \\ N(1) \\ N(2) \\ N(3) \\ N(4) \\ C(1) \\ C(2) \\ C(3) \\ C(4) \\ C(5) \\ C(5) \\ C(6) \\ C(7) \\ C(8) $	x 5179(4) 4292(5) 3090(5) 2879(5) 7270(4) 6221(4) 3635(3) 3370(4) 6130(4) 6903(4) 4753(8) 4013(5) 4634(5) 3178(5) 6546(4) 6336(5) 5079(5) 5920(6) 6399(5) 6025(5) 5199(4) 4728(4) 4566(4) 4245(5) 5799(5) 5199(4) 4728(4) 4566(4) 4245(5) 5199(5) 5199(4) 5199(5) 519(5) 519(5) 519(5) 519(5) 519(5) 519(5) 519(5) 519(5) 519(5) 519(5) 519(5) 519(5) 519(5) 5	y 4612(7) 6477(9) 9315(8) 8114(8) -1186(9) -2211(8) 2567(9) 5307(9) 3586(9) 4713(13) 2889(8) 5515(8) 8187(8) -1194(9) 3950(10) 2766(9) 2607(11) 1326(11) 163(10) 210(9) 1497(8) 4477(8) 4201(9) 5542(9)	z 7087(2) 7224(2) 5923(3) 5275(2) 6692(3) 7026(3) 6094(2) 6644(3) 6048(3) 5698(2) 5449(4) 4082(3) 6058(3) 5664(3) 6786(3) 6328(3) 6338(3) 6328(3) 6338(3) 6338(3) 6615(3) 6745(3) 6745(3) 6597(3) 6164(3) 5695(3) 5695(3)	$\begin{array}{c} 8,7(3)\\ 9,3(3)\\ 10,2(3)\\ 12,7(4)\\ 9,6(3)\\ 12,8(4)\\ 5,8(2)\\ 9,6(3)\\ 10,2(4)\\ 12,8(4)\\ 5,8(2)\\ 9,6(3)\\ 10,2(4)\\ 12,0(4)\\ 24,9(7)\\ 11,0(3)\\ 5,7(3)\\ 7,2(3)\\ 6,9(3)\\ 7,3(3)\\ 4,1(3)\\ 5,2(3)\\ 5,3(3)\\ 4,7(3)\\ 4,4(3)\\ 4,1(3)\\ 4,2(3)\\ 4,4(3)\\ 4,2(3)\\ 4,4(3)\\ 5,4(2)$
$\begin{array}{c} C(9) \\ C(10) \\ C(11) \\ C(12) \\ C(13) \\ C(14) \end{array}$	3789(5) 3652(5) 3922(5) 4379(4) 3848(4) 4369(5)	$\begin{array}{c c} 5512(9) \\ 6774(9) \\ 6776(9) \\ 5469(8) \\ 1527(8) \\ 2819(9) \end{array}$	$ \begin{vmatrix} 5532(3) \\ 5841(3) \\ 6300(3) \\ 6454(2) \\ 6745(3) \\ 5373(3) \end{vmatrix} $	$\begin{array}{c c} & 5,1(3) \\ & 5,0(3) \\ & 4,8(3) \\ & 4,1(3) \\ & 5,1(3) \\ & 6,6(3) \end{array}$
C(15) C(16)	2800(6) 3999(12)	$\begin{array}{c c} & 181(16) \\ & 1498(20) \end{array}$	$\begin{array}{ c c } & 7185(4) \\ & 4660(6) \end{array}$	$\begin{vmatrix} 7,6(4) \\ 10,5(7) \end{vmatrix}$

TABLE 1. Coordinates of the O, N, and C Atoms (×10<sup>4</sup>) and Equivalent Isotropic Temperature Factors (×10<sup>2</sup>, Å<sup>2</sup>)

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Bond lengths (Å) and angles of rotation in the I molecule.

lowing parameters: a = 16.141(3) Å, b = 8.292(1) Å, c = 27.953(4) Å, V = 3741(1) Å<sup>3</sup>, M = 450.3 ( $C_{16}H_{10}N_4O_{12}$ ), space group Pbca, Z = 8, and  $d_{calc}$  = 1.598 g/cm<sup>3</sup>. From a 0.12 × 0.25 × 0.25 mm crystal we measured 1203 reflections with I  $\geq 2\sigma(I)$ . All of the calculations were carried out by means of a set of SHELXTL programs with a NOVA-3 computer within the framework of the NICOLET R-3 system. The structure was determined by the direct method via the SOLV procedure and was refined by the complete-matrix method of least squares using the anisotropic temperature parameters for the C, N, and O atoms and the isotropic temperature parameters for the R factorwas 0.058 ( $R_W$  = 0.061). The coordinates of the nonhydrogen atoms and the equivalent isotropic temperature factors are presented in Table 1. It is apparent that the greatest errors are observed for the carbon atoms of the Me groups, as well as the carbonyl O(11) atom of the ester group with an extremely large U<sub>1SO</sub><sup>eq</sup> value (24.9 Å<sup>2</sup>), which may be associated with the partial disorderly character of this group.

The conformation of the I molecule is presented in Fig. 1. Because of the increased thermal mobility of the atom, particularly the terminal oxygen atoms and the atoms of the Me groups (see Table 1), the bond lengths in the molecule were determined with a low accuracy: 0.009-0.011 Å for O-N and O-C [0.014 Å for O(11)-C(14) and 0.018 Å for O(12)-C(16)] and 0.010-0.013 Å for C-C and C-N.

The dihedral angles between the aromatic rings in the ester and corresponding acid molecules have close values:  $81.1^{\circ}$  (I),  $87.1^{\circ}$  (II) [3], and  $78.8^{\circ}$  for 6,6'-dinitro-2,2'-dicarboxybiphenyl (III) [5]. In I the planar C(1)-C(6) (within the limits of 0.016 Å) and C(7)-C(12) (within the limits of 0.015 Å) are inclined toward the central biaryl C(1)-C(7) bond by angles of 2.2° and 1.0°, respectively. The most planar fragments of the carbomethoxy groups C(6)C(13)O(7)O(8) and C(8)C(14)O(11)O(12) are turned by 0.8° and 5.7°; C(15) and C(16) deviate from these planes by 0.090 Å and 0.180 Å. The methoxy groups have a trans orientation with respect to the C(1)-C(7) bond [torsion angles C(1)-C(6)-C(13)-O(7) and C(7)-C(8)-C(14)-O(12) are equal to -178.6° and 174.5°]. In complexes of 2-carboxybiphenyl 2'-(1,3-dioxolan-2-yl)methyl ester and 2,2'-dicarboxybiphenyl dimethyl ester with chromium tricarbonyl the angles of rotation of the carbomethoxy groups relative to the planes of the Ph rings are 2.7°, 9.4° and 33.8° [6]. The large value of the latter angle is possibly associated with the disordering of the ester group with respect to two positions. According to the data in [7], in the structures of benzoic acid esters the deviation of the plane of the ester group from the aromatic ring usually does not exceed 10°.

The bond lengths in the carbomethoxy group C(6)C(13)O(7)O(8)C(15) correspond to a greater extent to localized bonds (see Fig. 1) and are comparable to the values of the averaged geometrical parameters for benzoic acid esters [C=O 1.199(6) Å, C-O(CH<sub>3</sub>) 1.329(9) Å, O-CH<sub>3</sub> 1.448(8) Å, and  $C_{Ar}$ -C 1.484(12) Å [7]], as well as to the mean-statistical values [8] [1.202(9) Å, 1.337(13) Å, 1.454(12) Å, and 1.487(12) Å]. The too-short C(14)-O(11) and C(14)-O(12) distances and the significant deviation of the C(14) atom (0.081 Å) from the plane of the C(7)-C(12) ring may be associated with the partial disorderliness of the carbomethoxy group C(14)O(11)O(12)C(16). In the case of acids II and III we noted a tendency for delocalization of the C-O bonds, which is manifested in lengthening of the carbonyl bond to 1.227(5) Å and 1.232(5) Å (II) [3] and 1.213(5) Å [5] and shortening of the hydroxy bond to 1.288(5) Å and 1.284(5) Å (II) [3] and 1.296(4) Å (III) [5]. The indicated changes in the C-O bond lengths in the carboxy and carbomethoxy groups reflect the difference between the electron states of the atoms of these groups in the acids and esters [4, 9].

In the crystal the ester I molecules are oriented along the  $2_1$  axes parallel to the shortest b axis.

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CRYSTAL STRUCTURE OF 1,4,7,10-TETRAOXA-13-(4-ACETYLAMINOBENZO-SULFAMIDO)AZOCYCLOPENTADECANE

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A unique feature of crown ethers is their ability to form complexes both with metal cations and neutral proton donor molecules [1, 2]. These compounds hold potential in bioorganic chemistry as physiologically active compounds, receptor models, and highly selective complexing agents [3].

Examples have been described of the host-guest organization of complexes of sulfamides with crown ethers, when the active part of the molecule acting as the guest forms complexes by hydrogen bonding of the proton donor groups (NH, OH, or CH) in the substituent with the ethereal oxygen atoms of the host [4-6].

Special importance is found for crown ethers with an R group containing donor groups. According to Weber [7], such crown ethers belong to the lariat subgroup and, in many cases, have much greater complexing capacity than their unsubstituted analogs with R = H. In crystal chemistry, interest is found in the interaction of the donor groups of R with the ethereal oxygen atoms of the crown ether or of an adjacent molecule. In this case, host-guest complexes may be formed. For example, trans-diaminodibenzo-18-crown-6 has such structure [8].

We have studied a number of complexes with the following formula (see top of following page) [9-11], where a sandwich structure is formed when n = 2 with interaction of the NH<sub>2</sub> group of R and the ethereal oxygen atoms of the adjacent molecule [9]. When n = 1, the amino group is bound by the sulfamide oxygen atoms within the unit cell [10]. In previous work

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