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Organic peroxides are most commonly used for the generation of organic free radicals [1]. Structural studies and investigation of the relationship of structure and reactivity assist in the development of controlled synthetic reaction. In the present work, the Raman spectra of dibenzoyl peroxide (I) and 4,4'-dimethoxydibenzoyl peroxide (II) were studied and an x-ray diffraction structural study was carried out on (II) in order to determine the effect of substituents in dibenzoyl peroxide on its structural parameters.

Peroxide (II) consists of two approximately planar p-methoxyphenylcarboxylic fragments connected by a peroxide bond. The bond lengths and angles are given in Table 1. The angles between the planes of the $O^2C^7O^1$ and $O^{2'}C^{7'}O^{1'}$ carboxyl groups and the corresponding benzene rings are 2.7° and 8.8° . The OCH_3 substituents are located in the planes of the corresponding benzene rings (the dihedral angles $C^8O^3C^4C^3$ and $C^{8'}O^{3'}C^{4'}C^{3'}$ are $1.2(4)^\circ$ and $1.4(4)^\circ$, respectively). The angle between the planes of the benzene rings is 94.1° . The COOC torsion angle in (II) is $86.7(4)^\circ$, i.e., 4.3° less than the corresponding angle in (I) [2]. The geometrical parameters of the methoxyphenyl fragments in (II) are ordinary and close to those found for p-methoxybenzoic acid (III) [3] (deviations $\leq 3\sigma$).

TABLE 1. Bond Lengths and Bond Angles in 4,4'-Dimethoxydibenzoyl Peroxide*

Bond angle	d, Å	Bond angle	ω , deg
O^1-O^1	1.462(3)	$O^{1'}O^1C^7$	107,0(2)
O^1-C^7	1.394(4)	$O^1C^7O^2$	123,4(3)
O^2-C^7	1.182(4)	$O^1C^7C^1$	108,7(3)
C^2-C^7	1.470(4)	$O^2C^7C^1$	127,9(3)
C^1-C^2	1.390(4)	$C^7C^1C^2$	124,4(3)
C^2-C^3	1.391(4)	$C^7C^1C^6$	117,5(3)
C^3-C^4	1.366(4)	$C^2C^1C^6$	118,1(3)
C^4-C^5	1.385(4)	$C^1C^2C^3$	120,2(3)
C^5-C^6	1.345(5)	$C^2C^3C^4$	119,7(3)
C^1-C^6	1.387(5)	$C^3C^4C^5$	120,4(3)
O^3-C^4	1.358(4)	$C^4C^5C^6$	119,7(3)
O^3-C^8	1.428(5)	$C^1C^6C^5$	122,0(3)
$O^{1'}-C^{7'}$	1.402(4)	$O^3C^4C^3$	124,9(3)
$O^{2'}-C^{7'}$	1.184(4)	$O^3C^4C^5$	114,7(3)
$C^{1'}-C^{2'}$	1.473(4)	$C^4O^3C^8$	118,4(3)
$C^{1'}-C^{2'}$	1.383(4)	$O^1O^{1'}C^{7'}$	110,6(2)
$C^{2'}-C^{3'}$	1.372(4)	$O^{1'}C^{7'}O^{2'}$	122,8(3)
$C^{3'}-C^{4'}$	1.369(4)	$O^{1'}C^{7'}C^{1'}$	108,5(3)
$C^{4'}-C^{5'}$	1.392(4)	$O^{2'}C^{7'}C^{1'}$	128,6(3)
$C^{5'}-C^{6'}$	1.360(4)	$C^{7'}C^{1'}C^{2'}$	124,1(3)
$C^{1'}-C^{6'}$	1.376(5)	$C^{7'}C^{1'}C^{6'}$	118,2(3)
$O^{3'}-C^{4'}$	1.363(4)	$C^{2'}C^{1'}C^{6'}$	117,6(3)
$O^{3'}-C^{8'}$	1.443(4)	$C^{1'}C^{2'}C^{3'}$	122,0(3)
		$C^{2'}C^{3'}C^{4'}$	119,0(3)
		$C^{3'}C^{4'}C^{5'}$	120,1(3)
		$C^{4'}C^{5'}C^{6'}$	119,5(3)
		$C^{1'}C^{6'}C^{5'}$	121,8(3)
		$C^{1'}-C^{6'}$	124,9(3)
		$O^{3'}C^{4'}C^{5'}$	115,0(3)
		$C^{4'}O^{3'}C^{8'}$	117,8(2)

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

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TABLE 2. Atomic Coordinates ($\times 10^4$, $\times 10^3$ for H Atoms)

Atom	X	Y	Z	Atom	X	Y	Z
O ¹	2024(2)	1010(3)	4864(1)	C ^{5'}	-3215(3)	3919(4)	3630(2)
O ²	3023(3)	3290(3)	4428(1)	C ^{6'}	-2148(4)	3704(4)	4124(2)
O ³	7313(2)	1086(3)	6920(1)	C ^{7'}	48(4)	2532(4)	4541(2)
O ^{1'}	1004(3)	1420(3)	4283(1)	C ^{8'}	-4304(4)	2785(5)	1758(2)
O ^{2'}	112(3)	3062(3)	5147(1)	H ²	321(3)	-27(3)	588(1)
O ^{3'}	-4300(2)	3456(3)	2490(1)	H ³	506(3)	-71(3)	673(1)
C ¹	4120(3)	1782(4)	5406(2)	H ⁵	713(3)	317(3)	599(1)
C ²	4058(3)	479(4)	5890(2)	H ⁶	530(3)	360(3)	512(1)
C ³	5119(3)	206(4)	6408(2)	H ^{2'}	-20(3)	158(3)	316(1)
C ⁴	6225(3)	1223(4)	6436(2)	H ^{3'}	-199(3)	187(3)	224(1)
C ⁵	6304(3)	2508(4)	5947(2)	H ^{5'}	-404(3)	449(3)	376(1)
C ⁶	5276(4)	2766(4)	5447(2)	H ^{6'}	-219(3)	416(3)	454(1)
C ⁷	3054(4)	2180(4)	4842(2)	H ^{8.1}	652(4)	1(5)	775(2)
C ⁸	7307(4)	-193(6)	7452(2)	H ^{8.2}	815(3)	-11(4)	773(2)
C ^{1'}	-1013(3)	2808(4)	3957(2)	H ^{8.3}	716(4)	-130(5)	716(2)
C ^{2'}	-971(3)	2165(4)	3256(2)	H ^{8.1'}	-511(3)	312(3)	155(1)
C ^{3'}	-2021(3)	2380(4)	2742(2)	H ^{8.2'}	-346(3)	333(4)	148(2)
C ^{4'}	-3159(3)	3228(4)	2934(2)	H ^{8.3'}	-415(3)	162(4)	176(2)

The Raman spectra of diaroyl peroxides have a strong ν_{OO} band at 890 cm^{-1} [4], which is found for (I) and (II). The strong contribution of the peroxide bond to the redistribution of the potential energy of the vibration with frequency in the vicinity of 890 cm^{-1} is rather large ($\sim 40\%$), but there is no correlation between this frequency in a series of substituted diaroyl peroxides with the kinetic parameters for decomposition [4]. The ν_{OO} band for both (I) and (II) is found at 885 cm^{-1} , but their thermolysis in dioxane with 0.2 M styrene proceeds with activation energy equal to 125.5 and 121.4 kcal/mole , respectively, and rate constants at 80°C equal to $10^{-5.60}$ and $10^{-4.07}\text{ sec}$, respectively [5]. Our value for the O-O bond length in (II) ($1.462(3)\text{ \AA}$) is in accord with the data of Sax and McMullan [2] for (I), but such a comparison is unjustified due to the low precision in the determination of the geometrical parameters in (I).

The decrease in the $\nu_{\text{C=O}}$ frequency from 1788 cm^{-1} for (I) to 1778 cm^{-1} for (II) correlates with the decrease in the strength of the O-O bond strength in accord with the relationship noted in our previous work [4, 6].

The greater C=O bond length in (III) ($1.233(8)\text{ \AA}$) relative to (II) ($1.183(4)\text{ \AA}$) by 0.05 \AA is accompanied by a decrease in the $\nu_{\text{C=O}}$ frequency by 40 cm^{-1} : $\nu_{\text{C=O}}$ mean is 1778 cm^{-1} for (II) in CH_2Cl_2 and 1737 cm^{-1} for (III) in CCl_4 [7]. Thus, we should expect that the C=O bond in (II) should be longer than in (I). However, it was not possible to detect a difference in the C=O bond length for (II) ($1.183(4)\text{ \AA}$) found in the present work and the length of the corresponding bond in (I) ($1.185(20)\text{ \AA}$ [2]) due to the above-mentioned low precision of the results for (I).

EXPERIMENTAL

The unit cell parameters and the intensities of 2449 independent reflections for a $0.4 \times 0.4 \times 0.3\text{ mm}$ crystal of (II) were measured at 20°C on a Hilger-Watts Y/290 automatic four-circle diffractometer using $\text{Mo K}\alpha$ radiation, graphite monochromator, $\theta/2\theta$ scanning, and $(\sin \theta/\lambda)_{\text{max}} = 0.764$. The following unit cell parameters were found for monoclinic crystals of (II): $a = 9.778(1)$, $b = 8.2139(5)$, $c = 18.201(1)\text{ \AA}$, $\beta = 92.339(7)^\circ$, $V = 1460.6(2)\text{ \AA}^3$, $Z = 4$, space group $p2_1/n$, $M = 302.27$, $d_{\text{calc}} = 1.375\text{ g/cm}^3$, $\lambda(\text{Mo K}\alpha) = 0.71073\text{ \AA}$, $\mu(\text{Mo K}\alpha) = 0.15\text{ cm}^{-1}$. The arrangement of the molecules in the unit cell is shown in Fig. 1. A total of 1435 independent reflections with $I \geq 3\sigma(I)$ were used in the calculations.

The structure was solved by the direct method using the MULTAN program and refined by the method of least squares in the anisotropic approximation for the nonhydrogen atoms. The positions of the hydrogen atoms were calculated geometrically. The positions of the OCH_3 group hydrogen atoms were calculated assuming a staggered conformation. The positions of the hydrogen atoms were included in the refinement in the isotropic approximation. The final reliability factors were $R = 0.051$ and $R_w = 0.040$. The atomic coordinates are given in Table 2.* The calculations were carried out on an Eclipse S/200 computer using the INEXTL programs [8].

*The thermal parameters for the atoms may be obtained from the authors.

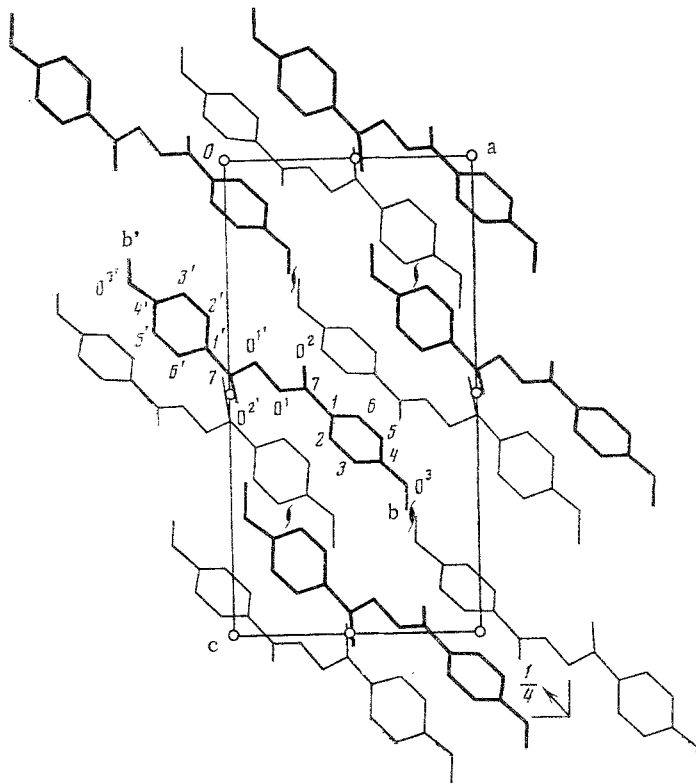


Fig. 1. Projection of the crystal structure of (II) along the b axis. The numbering of the atoms is given for the basis atom. Only numbers are given for the carbon atoms.

The Raman spectra of decimolar solutions of (I) and (II) in CH_2Cl_2 were taken on a Spex-Ramalog spectrometer with 3 cm^{-1} spectral slit width. The exciting radiation of an argon laser with $\nu\ 19,435\text{ cm}^{-1}$ was used.

CONCLUSIONS

An x-ray diffraction structural analysis gave the geometrical parameters of 4,4'-dimethoxydibenzoyl peroxide and dibenzoyl peroxide. The Raman spectra were also taken for these two peroxides. The introduction of electron-donor substituents into dibenzoyl peroxide causes a decrease in the COOC dihedral angle, $\nu\text{C=O}$ frequency and strength of the O—O bond with retention of the O—O and C=O bond lengths within experimental error.

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