

## The Synthesis and Structure of Bis(2,2'-bipyridine)- $\mu$ -methoxy- $\mu$ -nitrito-dinitritodicopper(II)

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The synthesis, chemophysical characterization and crystal structure of bis(2,2'-bipyridine)- $\mu$ -methoxy- $\mu$ -nitrito-dinitritodicopper(II) are reported. The compound crystallizes in the monoclinic system, space group  $C2/c$ , with  $a = 16.633$  (8),  $b = 8.320$  (6),  $c = 18.986$  (9) Å,  $\beta = 114.6$  (1)°,  $Z = 4$ . The structure was solved by standard heavy-atom Patterson and Fourier methods. A least-squares refinement, based on 1470 independent reflexions, reduced  $R$  to 0.048. The crystals consist of dimers formed by two  $[\text{Cu}(\text{NO}_2)(\text{bipy})]$  moieties bridged by one MeO and one  $\text{NO}_2$  group with a  $\text{Cu} \cdots \text{Cu}$  distance of 3.403 (1) Å. Each Cu atom has a slightly distorted tetragonal-pyramidal coordination. The basal atoms are the two bipyridine N atoms and two O atoms, one from the methoxy and one from the non-bridging nitrito group.

### Introduction

Recently we have studied some mixed  $\text{Cu}^I$  complexes of dinitrophenylmethane (Camus, Marsich & Mosca, 1976; Camus, Marsich, Nardin & Randaccio, 1975), nitrophenylmethane (Marsich & Camus, 1976) and nitromethane (Marsich & Camus, 1976; Camus, Marsich, Nardin & Randaccio, 1976) with tertiary phosphines or heterocyclic N donors. The complexes of nitrophenylmethane undergo a facile cleavage of the  $\text{PhCH=}$  group, with formation of nitrito complexes of  $\text{Cu}^I$ . The latter are easily and irreversibly oxidized by  $\text{O}_2$  in the case of complexes with N bases and the main autoxidation product of  $\text{Cu}(\text{bipy})\text{NPM}$  (NPM = nitrophenylmethane) in MeOH was found to correspond to the unexpected formula  $[\text{Cu}_2(\text{bipy})_2(\text{OCH}_3)(\text{NO}_2)_3]$  (I). Since, on the basis of its infrared and visible spectra, it seems to be a completely new compound among the numerous known nitrito complexes of  $\text{Cu}^{II}$  with bipy and phen (Marsich & Camus, 1976; Harris, Lockyer & Waterman, 1961; Procter, Hathaway, Billing, Dudley & Nicholls, 1969; Procter & Stephens, 1969; Stephens, 1969; Hathaway, Procter, Slade & Tomlinson, 1969) we thought it would be interesting to determine its solid-state structure.

### Experimental

#### Preparation

At first the complex was obtained by bubbling  $\text{O}_2$  for 18 h into a methanolic suspension of  $[\text{Cu}(\text{bipy})\text{NPM}]$  at room temperature. A green powder precipitated on concentration of the obtained solution and addition of ether. Later a more convenient route was found, namely the recrystallization from hot methanol of

$[\text{Cu}(\text{bipy})(\text{OH})]_2(\text{NO}_2)_2 \cdot 4\text{H}_2\text{O}$  (Marsich & Camus, 1976). The dark-blue crystals gave a deep-green solution, with a little green-blue residue, which was filtered off. From the clear solution deep-green crystals were formed on cooling which had a m.p. of 204–205°C (samples of some runs exploded at about 200°C). The calculated composition for  $\text{C}_{21}\text{H}_{19}\text{Cu}_2\text{N}_7\text{O}_7$  was C: 41.45, H: 3.14, Cu: 20.88, N: 16.11, MeOH: 5.26%; the composition found was C: 41.1, H: 3.00, Cu: 20.9, N: 15.9, MeOH: 5.5%. MeOH was determined by GLC after hydrolysis of the complex by NaOH, with benzene as internal standard and addition of bipy to facilitate solution of the complex. The conductivity at 25°C in MeOH was 129.8  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .

#### Crystal data

The crystal data are given in Table 1. Cell parameters were determined from Weissenberg and precession photographs taken with  $\text{Co } K\alpha$  radiation and refined by a least-squares fit of the diffractometer  $2\theta$ ,  $\chi$ ,  $\psi$  setting angles for 21 accurately centred reflexions in the  $2\theta$  range 21–38°. A prismatic crystal, about 0.41 × 0.23 × 0.70 mm, was mounted on a Siemens diffractometer and intensity data were collected by the

Table 1. *Crystal data*

$\text{C}_{21}\text{H}_{19}\text{Cu}_2\text{N}_7\text{O}_7$ , FW 608.5
Space group $C2/c$ (No. 15)
$a = 16.633$ (8), $b = 8.320$ (6), $c = 18.986$ (9) Å,
$\beta = 114.6$ (1)°
$U = 2388$ Å <sup>3</sup> , $Z = 4$
$D_m = 1.71$ (by flotation), $D_x = 1.69$ g cm <sup>-3</sup>
Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
$\mu$ (Mo $K\alpha$ ) = 19.4 cm <sup>-1</sup> , $F(000) = 1232$

$\theta$ - $2\theta$  scan mode with Mo  $K\alpha$  radiation to a  $2\theta$  (max.) of  $54^\circ$ . The reflexions with  $I_o < 3\sigma(I_o)$  were rejected; the remainder (1470) were corrected for Lorentz-polarization factors and were used in the subsequent calculations. No absorption correction ( $\mu\bar{r} = ca\ 0.6$ ) was applied.

### Structure determination and refinement

The structure was solved by conventional Patterson and Fourier methods. The centrosymmetric space group  $C2/c$  was assumed and its choice was confirmed by the subsequent successful refinement. Least-squares isotropic refinement reduced  $R$  to 0.081. After anisotropic refinement, a three-dimensional difference Fourier synthesis was calculated to locate the H atoms. Calculated positions ( $C-H = 1.08\ \text{\AA}$ ) of these occurred in regions of positive electron density for all atoms, with the exception of the three H atoms of the methoxy group, which appeared to be disordered.

The final anisotropic block-diagonal least-squares refinement gave  $R = 0.048$ . The coordinates and temperature factors of the H atoms ( $B$  was set at  $5.0\ \text{\AA}^2$ ) were not allowed to vary. The final weighting scheme

was  $w = 1/(A + B|F_o| + C|F_o|^2)$ , where  $A = 11.0$ ,  $B = 1.0$  and  $C = 0.004$  were chosen to maintain  $w(|F_o| - |F_c|)^2$  essentially constant over all ranges of  $|F_o|$  and  $\sin \theta/\lambda$ . The numbering scheme for the atoms is shown in Fig. 1. Final atomic parameters are listed in Table 2, bond lengths and angles in Table 3 and equations of some least-squares planes, with the displacements of

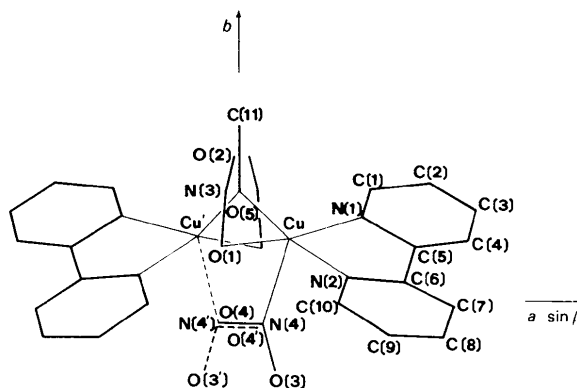


Fig. 1. A view of the molecule showing the atom-numbering scheme.

Table 2. Fractional coordinates ( $\times 10^4$ ) and anisotropic temperature factors ( $\times 10^4$ ), with estimated standard deviations in parentheses

$\beta_{ij}$  are the coefficients in the expression:  $\exp[-(\beta_{11}h^2 + \beta_{12}hk + \beta_{13}hl + \beta_{22}k^2 + \beta_{23}kl + \beta_{33}l^2)]$ .

#### (a) Non-hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{12}$	$\beta_{13}$	$\beta_{22}$	$\beta_{23}$	$\beta_{33}$
Cu	742 (0)	1557 (1)	3445 (0)	33 (0)	-4 (1)	34 (0)	138 (1)	7 (1)	33 (0)
O(1)	-280 (3)	1265 (8)	3789 (3)	63 (2)	26 (9)	56 (3)	285 (12)	27 (8)	52 (2)
O(2)	134 (4)	3517 (9)	4199 (4)	72 (3)	-60 (11)	49 (4)	357 (14)	-53 (10)	61 (2)
O(3)	523 (7)	-2037 (15)	3021 (7)	85 (5)	157 (18)	37 (8)	226 (22)	104 (18)	74 (5)
O(4)	-373 (6)	-762 (14)	2152 (6)	143 (4)	-2 (16)	122 (5)	96 (19)	26 (14)	66 (4)
O(5)	0 (0)	2662 (7)	2500 (0)	36 (2)	0 (0)	22 (3)	116 (8)	0 (0)	34 (2)
N(1)	1897 (3)	1971 (6)	3329 (3)	35 (2)	-16 (6)	34 (2)	146 (8)	-6 (6)	34 (2)
N(2)	1619 (3)	558 (7)	4447 (3)	44 (2)	-2 (7)	41 (2)	151 (9)	9 (6)	37 (2)
N(3)	-373 (4)	2489 (10)	4143 (4)	56 (2)	-16 (11)	54 (3)	315 (15)	-19 (10)	50 (2)
N(4)	380 (7)	-760 (16)	2864 (7)	142 (5)	-28 (17)	126 (6)	37 (19)	18 (16)	74 (4)
C(1)	1974 (4)	2763 (9)	2732 (4)	49 (2)	-36 (9)	44 (3)	185 (10)	-0 (8)	37 (2)
C(2)	2795 (4)	2937 (10)	2696 (4)	52 (2)	-39 (10)	57 (3)	222 (12)	-17 (9)	43 (2)
C(3)	3543 (4)	2260 (11)	3273 (4)	44 (2)	-22 (11)	54 (3)	239 (14)	-28 (10)	49 (2)
C(4)	3460 (4)	1401 (9)	3878 (4)	41 (2)	-5 (10)	43 (3)	212 (13)	-8 (9)	43 (2)
C(5)	2623 (4)	1307 (7)	3890 (3)	35 (2)	-10 (7)	28 (3)	139 (10)	-17 (7)	35 (2)
C(6)	2464 (4)	483 (8)	4521 (4)	40 (2)	-25 (8)	27 (3)	143 (9)	-12 (7)	33 (2)
C(7)	3121 (4)	-286 (9)	5145 (4)	43 (3)	-21 (10)	15 (4)	188 (11)	16 (9)	42 (3)
C(8)	2907 (5)	-964 (10)	5724 (5)	56 (3)	-51 (11)	7 (5)	190 (11)	30 (10)	40 (2)
C(9)	2054 (5)	-870 (10)	5658 (4)	64 (3)	-39 (11)	35 (4)	210 (12)	23 (9)	40 (2)
C(10)	1414 (4)	-109 (9)	5002 (4)	56 (3)	-16 (10)	51 (3)	200 (12)	25 (8)	42 (2)
C(11)	0 (0)	4394 (11)	2500 (0)	44 (4)	0 (0)	41 (5)	156 (14)	0 (0)	50 (3)

#### (b) Calculated hydrogen atom coordinates ( $\times 10^4$ ): hydrogen atoms are numbered according to the atom to which they are bonded

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
H(C1)	1396	3263	2281	H(C7)	3781	-362	5185
H(C2)	2844	3585	2229	H(C8)	3406	-1549	6213
H(C3)	4176	2390	3258	H(C9)	1880	-1365	6096
H(C4)	4022	833	4319	H(C10)	745	-55	4940

Table 3. Bond distances (Å), bond angles (°) and their estimated standard deviations

Cu—O(1)	2.074 (6)	N(2)—C(6)	1.354 (9)
Cu—O(2)	2.634 (8)	N(2)—C(10)	1.354 (10)
Cu—O(5)	1.934 (3)	N(4)—O(4)	1.408 (13)
Cu—N(1)	2.052 (6)	C(1)—C(2)	1.403 (11)
Cu—N(2)	2.030 (5)	C(2)—C(3)	1.389 (9)
Cu—N(4)	2.177 (13)	C(3)—C(4)	1.408 (12)
O(1)—N(3)	1.265 (11)	C(4)—C(5)	1.404 (10)
O(2)—N(3)	1.174 (11)	C(5)—C(6)	1.497 (10)
O(3)—N(4)	1.103 (18)	C(6)—C(7)	1.388 (8)
O(5)—C(11)	1.441 (11)	C(7)—C(8)	1.407 (13)
N(1)—C(1)	1.363 (10)	C(8)—C(9)	1.373 (12)
N(1)—C(5)	1.351 (7)	C(9)—C(10)	1.407 (9)
O(1)—Cu—O(2)	49.5 (2)	Cu—N(2)—C(6)	115.1 (5)
O(1)—Cu—O(5)	93.3 (1)	Cu—N(2)—C(10)	125.5 (4)
O(1)—Cu—N(1)	168.7 (2)	C(6)—N(2)—C(10)	119.2 (5)
O(1)—Cu—N(2)	91.1 (2)	O(1)—N(3)—O(2)	113.1 (8)
O(1)—Cu—N(4)	88.1 (4)	Cu—N(4)—O(3)	137.2 (10)
O(2)—Cu—O(5)	88.2 (2)	Cu—N(4)—O(4)	115.8 (9)
O(2)—Cu—N(1)	122.9 (2)	O(3)—N(4)—O(4)	105.2 (11)
O(2)—Cu—N(2)	91.9 (2)	N(1)—C(1)—C(2)	121.4 (5)
O(2)—Cu—N(4)	137.4 (2)	C(1)—C(2)—C(3)	119.3 (7)
O(5)—Cu—N(1)	94.8 (1)	C(2)—C(3)—C(4)	119.3 (7)
O(5)—Cu—N(2)	174.2 (2)	C(3)—C(4)—C(5)	118.5 (5)
O(5)—Cu—N(4)	90.9 (3)	N(1)—C(5)—C(4)	122.1 (6)
N(1)—Cu—N(2)	80.2 (2)	N(1)—C(5)—C(6)	114.8 (6)
N(1)—Cu—N(4)	99.7 (4)	C(4)—C(5)—C(6)	123.1 (5)
N(2)—Cu—N(4)	92.9 (3)	N(2)—C(6)—C(5)	114.7 (5)
Cu—O(1)—N(3)	111.8 (5)	N(2)—C(6)—C(7)	121.5 (7)
Cu—O(2)—N(3)	85.6 (6)	C(5)—C(6)—C(7)	123.7 (7)
Cu—O(5)—Cu'	123.2 (3)	C(6)—C(7)—C(8)	119.1 (7)
Cu—O(5)—C(11)	118.4 (2)	C(7)—C(8)—C(9)	119.6 (7)
Cu—N(1)—C(1)	126.0 (4)	C(8)—C(9)—C(10)	118.5 (8)
Cu—N(1)—C(5)	114.6 (5)	N(2)—C(10)—C(9)	122.0 (7)

Table 4. Equations of least-squares planes and, in square brackets, distances (Å) of atoms from the planes

The equations are referred to the crystal axes and  $x, y, z$  are fractional coordinates.

Plane 1: Cu, Cu', O(4), O(5), N(4)  
 $15.778x - 0.017y - 12.960z = -3.243$

[Cu -0.054, Cu' 0.054, O(4) -0.133, O(5) -0.001, N(4) 0.133]

Plane 2: Cu, O(1), O(5), N(1), N(2)  
 $-0.596x + 7.340y + 8.387z = 4.066$

[Cu -0.078, O(1) 0.057, O(5) -0.015, N(1) 0.060, N(2) -0.023]

Plane 3: N(1), N(2), C(1) to C(10)  
 $-0.106x + 1.630y + 9.098z = 4.376$

[N(1) -0.031, N(2) -0.010, C(1) -0.013, C(2) 0.041,  
 C(3) 0.048, C(4) -0.011, C(5) -0.029, C(6) -0.035,  
 C(7) -0.047, C(8) 0.006, C(9) 0.053, C(10) 0.029]

relevant atoms from them, in Table 4.\* Atomic scattering factors were calculated as usual (Moore, 1963).

All calculations were carried out on a CDC 6200 computer with the programs described previously (Albano, Domenicano & Vacigato, 1966).

## Results and discussion

The crystals are built up of dimers formed by two [Cu(NO<sub>2</sub>)(bipy)] moieties, related by a twofold crystallographic C<sub>2</sub> symmetry axis and bridged by one MeO and one NO<sub>2</sub> group. The MeO group, lying along the C<sub>2</sub> axis, binds both Cu atoms through its O atom; the NO<sub>2</sub> bridge has the unsymmetrical arrangements shown in Fig. 2, with a half-occupancy of the two possible orientations (a) and (b).

The CuNOCu cycle is nearly planar.

The coordination polyhedron around the Cu atom can be described as a slightly distorted square pyramid. Two of its equatorial sites are occupied by the bipyridine N atoms, the others by one methoxo and one  $\sigma$ -bonded nitrito group, whereas the axial position is occupied in turn by the N or one O atom of a  $\mu$ -nitrito group. The Cu...Cu distance [3.403 (1) Å] is significantly longer than that in  $\mu$ -oxo-bridged Cu complexes (2.847–3.000 Å) (Hodgson, 1975). This is obviously because of the presence of the bulky nitrito bridge, which causes the Cu atoms to stay further apart, as in the octahedral Co<sup>III</sup> complex [(NH<sub>3</sub>)<sub>4</sub>Co(NH<sub>2</sub>)(NO<sub>2</sub>)Co(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>4</sub>·4H<sub>2</sub>O (Co...Co = 3.279 Å), where a similar double bridge is present (Thewalt & Marsh, 1970). Comparable Cu...Cu distances are also present in pyridine *N*-oxide complexes (3.2–3.5 Å) in which, however, the Cu—O bond distances are largely non-equivalent (Andrew & Blake, 1973, and references therein). The Cu—OMe distance [1.934 (3) Å] is not affected by the large Cu...Cu distance and is comparable with the mean value (1.927 Å) found in binuclear Cu complexes containing two hydroxo bridges (Majeste & Meyers, 1970; Casey, Hoskins

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32296 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

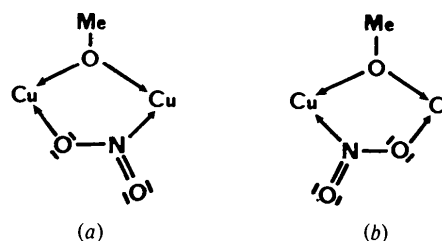


Fig. 2. The unsymmetrical arrangements of the NO<sub>2</sub> bridge.

& Whillans, 1970; Lewis, Hatfield & Hodgson, 1972). Furthermore, the Me—O distance [1.44 (1) Å] is in agreement, within the e.s.d., with that of a C—O single bond [MeOH 1.428 (3), Me—O—Me 1.416 (3) Å] (Sutton, 1965). The N—O bond distances [1.41 (1) and 1.10 (2) Å] are those of a single and double bond respectively (Padmanabhan, Smith & Peterson, 1967; Sutton, 1965), in agreement with Fig. 2. The other two NO<sub>2</sub> groups are asymmetrically localized around the Cu atoms [Cu—O(1) 2.074 (6), Cu—O(2) 2.634 (8) Å]. The weak Cu—O bond (Brown, Lee, Melsom, Hathaway, Procter & Tomlinson, 1967) and the O(1)—N(3)—O(2) angle of 113.1 (8)° (Stephens, 1969) suggest a 'semi-coordination' of the NO<sub>2</sub> groups to the metal atom. Consequently there are also different N—O bond distances [O(1)—N(3) 1.265 (11), O(2)—N(3) 1.174 (11) Å], the O atom more strongly bonded to Cu giving rise to a longer N—O bond. Conductivity measurements indicate that a partial dissociation of the 'semi-coordinated' NO<sub>2</sub> groups occurs in methanol solution. In a basic medium there is also substitution of the two Cu bridging groups by hydroxo groups, as proved by the detection of free methanol and by the isolation of crystals of [Cu(bipy)(OH)NO<sub>2</sub>]<sub>2</sub>·4H<sub>2</sub>O (Marsich & Camus, 1976) from the solution.

Each bipyridine ligand acts as a symmetric bidentate chelate through the N atoms. The Cu—N bond distances [Cu—N(1) 2.052 (6), Cu—N(2) 2.030 (5) Å] and the N(1)—Cu—N(2) angle [80.2 (2)°] are in good agreement with the values found for other Cu<sup>II</sup> complexes with bipyridine and phenanthroline (Thewalt & Marsh, 1970; McFadden & McPhail, 1975). The bipyridine molecules also show usual bond distances and angles. Each of the six-membered rings of the bipyridine group is planar, with no atom being displaced more than 0.01 Å from its least-squares plane, but they are slightly mutually twisted about the 2,2'-carbon bond (dihedral angle 3.7°). The bipyridine molecule is approximately normal to the plane containing the double bridge (dihedral angle 100.6°). This situation is different from that observed in [Cu(bipy)(OH)]<sub>2</sub>SO<sub>4</sub>·5H<sub>2</sub>O (Casey, Hoskins & Whillans, 1970) and [Cu(bipy)(OH)NO<sub>3</sub>]<sub>2</sub> (Majeste & Meyers, 1970), where the bipyridine N atoms and the O atoms involved in the  $\mu$  double bridge lie in the basal plane. In the present case the steric interaction between the Me—O group and the H(C1) atom hinders the arrangement observed in the two above complexes, where the two bipyridyl rings are approximately coplanar. In contrast, in the present structure the two bipyridine ligands are markedly bent (mean dihedral angle 62.0°), allowing efficient phenyl—phenyl-type contacts among bipyridine molecules of different dimers.

The IR spectrum of complex I shows, in addition to the peaks from the coordinated bipyridine, main absorption bands at about 1374 *s, br*; 1230 *s, br*; 1155 *s, br*; 904 *m, d* (a sharp band superimposed on a broad

one); 542 *m, br*; and 330 *m, br* cm<sup>-1</sup>. On the basis of the structure found and a comparison with spectra of related complexes, the above frequencies have been tentatively assigned as follows: 1374 and 1155 cm<sup>-1</sup>:  $\nu(\text{NO}_2)_{\text{asym}}$  and  $\nu(\text{NO}_2)_{\text{sym}}$  respectively of the semi-coordinated NO<sub>2</sub> groups (Hathaway, Procter, Slade & Tomlinson, 1969); 1230 cm<sup>-1</sup>:  $\nu(\text{NO}_2)_{\text{sym}}$  of the bridging NO<sub>2</sub> group (Goodgame & Hitchman, 1967); broad band at 904 cm<sup>-1</sup>:  $\nu(\text{CO})$  of the MeO group (usually found at higher frequencies: Andrew, Blake & Fraser, 1976); 542 cm<sup>-1</sup> (split):  $\nu(\text{CuO})$  [shifted to higher values with respect to those found for  $\mu$ -dihydroxocopper derivatives (Ferraro & Walker, 1965)]; 330 cm<sup>-1</sup>:  $\nu(\text{Cu-bridging NO}_2)$ . The electronic reflectance spectrum of the complex shows only a broad asymmetric band, characteristic of the envelopment of *d-d* transitions. Its maximum, at *ca* 670 nm, is in agreement with the pentacoordination found to be present (Gibson & McKenzie, 1971, and references therein). The maximum shifts to 645 nm in methanol or water, probably because of coordination of the solvent to the sixth position on the Cu atoms, and to 613 nm in a diluted sodium hydroxide solution, where the hydrated [(bipy)-Cu(OH)]<sub>2</sub><sup>+</sup> species is formed (see also Harris, Sinn, Walker & Woolliams, 1968).

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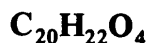
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## Conformational Studies of Oligomethylene Glycol Derivatives and Related Compounds. VI. The Crystal and Molecular Structure of Hexamethylene Glycol Dibenzoate,



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The diester hexamethylene glycol dibenzoate,  $\text{C}_{20}\text{H}_{22}\text{O}_4$ , crystallizes in the orthorhombic space group *Pbca* with four molecules per unit cell of dimensions  $a = 8.728$  (3),  $b = 19.676$  (5),  $c = 10.551$  (3) Å. The structure, solved by direct methods, was refined by block-diagonal least squares to a final  $R_w$  value of 0.049. The molecule, which has a crystallographic centre of symmetry, is in the all-*trans* conformation. The molecules are packed in a herring-bone manner. Van der Waals interactions maintain the molecules together in the crystal. The conformational resemblance of this molecule to the polymer poly(hexamethylene glycol terephthalate) is discussed.

### Introduction

One method of determining polymer structures is to study crystal structures of small related molecules or oligomers. This provides accurate information about the molecular geometry of these model compounds. Bond lengths and angles, specific to the chemical species studied, are used as standards for further conformational analysis and as constraints in the least-squares refinement of polymer structures. Previous research has shown some evidence that the solid-state conformation of the polymer could be close to that of the related model compound or oligomer. However, because of the difficulty of obtaining good oligomer crystals (in the case of biopolymers) or perhaps as a result of some lack of communication between polymer crystallographers and single-crystal crystallographers, this approach has not yet been fully explored. In order to investigate the similarities or differences between the solid-state conformation of the polymer and that of the related model compound we have undertaken a sys-

tematic study of oligomethylene glycol derivatives related to the poly(oligomethylene terephthalates):  $[\text{O}-(\text{CH}_2)_p-\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}]_n$ , with  $p = 2$  to 10. For ethylene glycol dibenzoate (Pérez & Brisse, 1976*a*), trimethylene glycol dibenzoate and trimethylene glycol di-*p*-chlorobenzoate (Pérez & Brisse, 1977, 1976*b*) the conformations were found to be closely related to those of the polymers poly(ethylene terephthalate) and poly(trimethylene terephthalate) respectively.

As a continuation of our systematic studies of oligomethylene glycol derivatives, we present here the crystal and molecular structure of hexamethylene glycol dibenzoate, which is considered to be a model compound for poly(hexamethylene glycol terephthalate):  $[\text{O}-(\text{CH}_2)_6-\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}]_n$ .

### Experimental

Crystals of hexamethylene glycol dibenzoate,  $\text{C}_{20}\text{H}_{22}\text{O}_4$ , were obtained by slow evaporation of an