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Conformational Studies of Oligomethylene Glycol Derivatives and Related Compounds. VIII. The Crystal and Molecular Structure of Diphenyl Succinate, $C_{16}H_{14}O_4$

BY FRANÇOIS BRISSE, NORMAND MOLHANT AND SERGE PÉREZ*

Département de Chimie, Université de Montréal, Montréal, Canada H3C 3V1

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Abstract

The crystal structure of diphenyl succinate, $C_{16}H_{14}O_4$, has been solved by direct methods from 1089 reflections collected on a Syntex $P1$ diffractometer. The final R_w value is 0·046. The crystals belong to the space group $P2_1/c$ and have a unit cell of dimensions $a = 9{\cdot}096$ (3), $b = 5{\cdot}688$ (2), $c = 13{\cdot}305$ (5) Å and $\beta = 93{\cdot}26$ (2)°. The molecule consists of three planar moieties: the succinate group and the two phenyl groups which are at 67·7° from the succinate part of the molecule.

Introduction

We have undertaken a systematic study on the structures of a series of oligomethylene dibenzoates and *para*-substituted dibenzoates: XC_6H_4–CO–O–$(CH_2)_x$–O–CO–C_6H_4X with X = H, Cl, NO_2 and x = 2, 3, 4, 5, 6 and 10 (Brisse & Pérez, 1976; Pérez & Brisse, 1977*a*,*b*). These are model compounds for the related poly(oligomethylene terephthalates): $[C_6H_4$–CO–O–$(CH_2)_x$–O–CO$]_n$, the best known of which is Terylene or Dacron ($x = 2$). Some unusual geometrical features were revealed by this study. For example, the bond distances between methylene groups were observed to be systematically shorter than the expected distance for this type of bond while the –O–CH_2–CH_2 bond angles were not as open as expected.

It is to find an explanation for these unexpected features that the determination of the crystal structure of diphenyl succinate has been undertaken. As can be noted in Fig. 1 the two molecules are positional isomers since only the order of O and C=O atoms surrounding the methylene groups is reversed, changing from ethylene glycol dibenzoate (I, with X = H, $x = 2$) to diphenyl succinate (II).

Experimental

Diphenyl succinate was prepared by a reaction between phenol and succinyl chloride in the presence of pyridine, following the method described by Heim & Poe (1944). Clear well-developed prismatic crystals were obtained by slow evaporation of a methanol solution at room temperature. Photographic work and intensity data were obtained from a crystal of dimen-

* Present address: Centre de Recherches sur les Macromolécules Végétales, CNRS, 53X, Grenoble, France.

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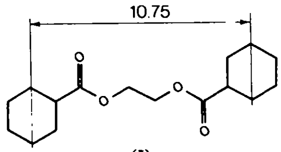
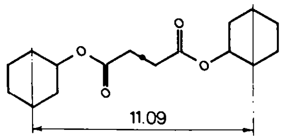


(I)



(II)

Fig. 1. The chemical structure of ethylene glycol dibenzoate (I) and diphenyl succinate (II). The numerical values given are the fiber repeats predicted for the polymers if they and their parent model compounds have the same conformations.

sions $0{\cdot}2 \times 0{\cdot}3 \times 0{\cdot}5$ mm mounted with its c axis approximately coinciding with the φ axis of the diffractometer. Weissenberg and precession photographs indicated that the crystal belongs to the monoclinic system and the systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) show the space group to be $P2_1/c$. The density was obtained by the flotation method. The unit-cell dimensions, obtained as part of the crystal alignment on the Syntex $P\bar{1}$ diffractometer by a least-squares fit to the settings of 12 well-centered reflections, are listed in Table 1 with other crystal data of interest.

The intensities of the 2016 independent reflections within one quadrant of the Mo sphere limited by $2\theta \leq 50°$ were measured by the θ–2θ technique using graphite-monochromatized Mo radiation. A variable scan rate [1 to 24° (2θ) min^{-1}] was used with a scan width of 1·2° (2θ) below $K\alpha_1$ and above $K\alpha_2$. The background was measured at each end of the scan range and the background time to scan time ratio was 0·40. The intensities of three reference reflections, monitored every 50 measurements, decreased by only 5% of their initial values over the duration of the data collection. The data reduction, using the programs of Ahmed, Hall, Pippy & Huber (1973), took this decline into account. The standard deviation $\sigma(I)$ for the net intensity I_N of a reflection was calculated by a relation given in Brisse, Lectard & Schmidt (1974). Of the 2016 measured reflections, 927 were assigned zero intensity since $I_N/\sigma(I) \leq 1{\cdot}96$. The data were corrected for Lorentz and polarization effects in the usual manner. Since the absorption coefficient was only 0·078 mm^{-1}, the data were not corrected for absorption.

Table 1. *Crystal data*

$C_{16}H_{14}O_4$, $M_r = 270{\cdot}29$, m.p. 393–394 K, $F(000) = 284$ e, $a = 9{\cdot}096$ (3), $b = 5{\cdot}688$ (2), $c = 13{\cdot}305$ (5) Å, $\beta = 93{\cdot}26$ (2)°, $V = 687{\cdot}3$ Å^3, $P2_1/c$, $Z = 2$, $d_{obs} = 1{\cdot}31$, $d_{calc} = 1{\cdot}306$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·078 mm^{-1}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å.

Structure determination and refinement

A set of normalized structure factors E was obtained after isotropic temperature factor correction. The structure was solved by the *MULTAN* program* which generated 1305 $\sum_2$ relationships using all E's down to 1·70. Among the eight sets of phases that were developed, two converged toward the same solution. The resulting E map revealed all the non-hydrogen atoms. Least-squares refinement of the atomic coordinates with individual isotropic temperature factors brought the R factor ($R = \sum \Delta F/\sum F_0$) to 0·15. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where w is inversely proportional to the variance derived from the value of $\sigma(I)$: $w = 1/\sigma^2(F)$. The refinement process was continued by the block-diagonal approximation with anisotropic temperature factors. All the H atoms found on the following Fourier difference synthesis were included, with isotropic temperature factors, in the least-squares refinement. At the end of the refinement the average parameter shift was less than $0{\cdot}4\sigma$. The final Fourier difference map showed no significant residual electron density. The extreme fluctuations ranged from $-0{\cdot}28$ to $+0{\cdot}25$ e Å^{-3}. The final R_w value [$R_w = (\sum w\Delta F^2/\sum wF_o^2)^{1/2}$] reached 0·046 and the standard deviation of unit weight σ_F was 2·61 {$\sigma_F = [\sum w\Delta F^2/(m-n)]^{1/2}$, with m = number of reflections and n = number of refined parameters}. When all measured reflections were included, $R_w = 0{\cdot}047$. The corresponding R values were 0·048 and 0·072 respectively. The X-ray scattering factors were obtained from Cromer & Waber (1965) for C and O atoms, and from Stewart, Davidson & Simpson (1965) for H atoms.†

Results and discussion

Since there were only two molecules per unit cell, the middle of the CH_2–CH_2 bond of diphenyl succinate had to be on a crystallographic center of symmetry. The stereochemical structure of a complete molecule is shown in Fig. 2. The positional parameters with their standard deviations are presented in Table 2.

* The computer programs used were locally modified versions of the following: *NRC*-2: data reduction, modified to include the polarization due to the monochromator; *NRC*-14: error analysis and agreement summary; *NRC*-22: least-squares plane (Ahmed *et al.*, 1973); *FORDAP*: Fourier and Patterson maps (A. Zalkin); *NUCLS*: least-squares refinement (R. J. Doedens & J. A. Ibers) with block-diagonal approximation option; *MULTAN*: multi-solution program (Germain, Main & Woolfson, 1971); **TLS**: rigid-body analysis (Schomaker & Trueblood, 1968); *ORTEP*: stereodrawings (Johnson, 1965).

† Lists of structure factors, thermal parameters and mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34381 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional coordinates and their e.s.d.'s* ($\times 10^4$, *for* H $\times 10^3$) *and* U_{eq} ($\times 10^3$ *for* O *and* C) *and* U_{iso} ($\times 10^3$ *for* H)

	x	y	z	U_{eq}/U_{iso} (Å^2)
O(1)	7106 (2)	10836 (5)	3921 (2)	69 (4)
O(2)	6126 (2)	7577 (5)	3209 (1)	54 (2)
C(1)	7155 (3)	7561 (6)	2453 (2)	42 (6)
C(2)	8136 (3)	5734 (7)	2451 (2)	52 (5)
C(3)	9099 (3)	5626 (8)	1680 (3)	62 (10)
C(4)	9059 (4)	7314 (8)	946 (2)	64 (10)
C(5)	8061 (4)	9112 (8)	960 (2)	62 (10)
C(6)	7101 (3)	9251 (7)	1725 (3)	55 (4)
C(7)	6189 (3)	9351 (7)	3891 (2)	44 (4)
C(8)	4951 (3)	9100 (6)	4584 (2)	46 (4)
H(2)	817 (3)	461 (6)	301 (2)	66 (4)
H(3)	983 (3)	434 (6)	171 (2)	85 (5)
H(4)	966 (3)	727 (6)	42 (2)	62 (4)
H(5)	796 (3)	1025 (6)	44 (2)	57 (4)
H(6)	639 (3)	1049 (6)	174 (2)	61 (4)
H(81)	399 (3)	921 (5)	416 (2)	51 (4)
H(82)	499 (3)	760 (6)	484 (2)	47 (4)

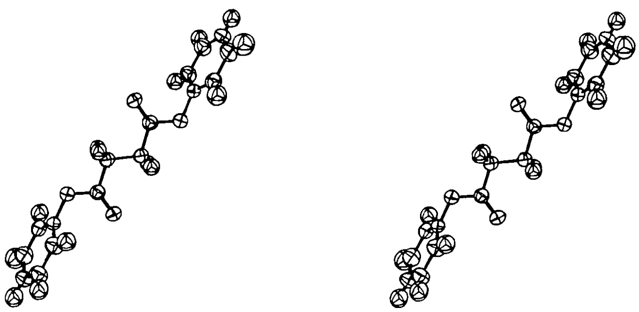


Fig. 2. Stereoscopic pair showing one molecule of diphenyl succinate.

The standard deviations of the interatomic bond distances and angles, derived from the e.s.d.'s of the fractional coordinates, amount to 0·003–0·006 Å and 0·2–0·3° respectively for non-hydrogen atoms and to 0·03 Å for bond distances involving H atoms.

All bond distances and angles, as shown in Fig. 3, are reasonable and compare extremely well with those obtained for ethylene glycol dibenzoate (Pérez & Brisse, 1976). However, the CH_2—CH_2 bond distance which was short in ethylene glycol dibenzoate is also short in the succinate group.

Rigid-body analysis

To ensure that the observed short distance in the succinate group is significant, a rigid-body analysis has been undertaken by the **TLS** method described by Schomaker & Trueblood (1968). When the molecule is considered as a whole, the root mean square of the ΔU_{ij}'s is 0·0071 Å^2, a value slightly greater than $3\sigma(U_{ij})$. Consequently the molecule cannot be considered as a rigid body. However, when the phenyl group [C(1) to C(6) and O(2)] and the succinate group [O(1), O(2), C(7) and C(8)] are considered separately, the values of the root-mean-square ΔU_{ij} are 0·0011 and 0·0023 Å^2 respectively. Thus it can be said that the two groups are rigid and that they move independently of each other. The rigid-body correction of the bond distances in the succinate group resulted in a general lengthening of the bonds by only 0·003 Å. Thus the short CH_2—CH_2 bond is a real feature of the structure.

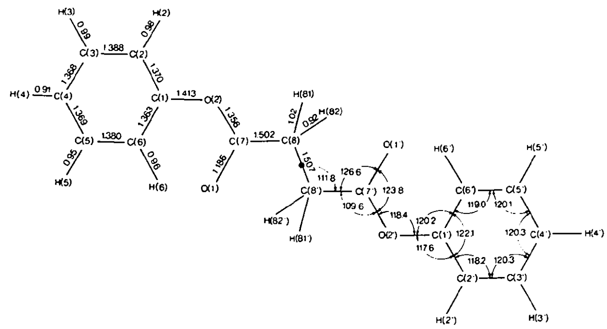


Fig. 3. Bond distances (Å), angles (°) and numbering of the atoms of diphenyl succinate.

One of the reasons this work was undertaken was the unusual bond distances and angles around the ethylenic group in various glycol dibenzoates. These distances are compared in Table 3 with those in diphenyl succinate and a number of compounds containing succinate groups or ions or having an ethylenic sequence of atoms.

The CH_2—CH_2 bond length, whose average value in the succinate groups is 1·515 (13) Å, is half-way between the usually quoted Csp^3—Csp^3 distance of 1·537 (5) Å (Sutton, 1965) and the average value of 1·489 (17) Å in the glycol dibenzoates. The data in Table 3 reveal that the extremely short CH_2—CH_2 bond distances occur only when the atoms adjacent to the ethylenic group are either O or S. The CO—CH_2—CH_2 bond angles in the succinate groups with an average value of 113 (2)° are normal but differ significantly from the O—CH_2—CH_2 angles in the glycol dibenzoates whose average is 107 (2)°. These effects are independent of the conformation adopted by the X—CH_2—CH_2—Y sequence of atoms. The observations are comparable to recent reports of the effects of halogen atoms and other substituents on the bond distances and angles of a phenyl group (Brisse & Sygusch, 1974; Domenicano, Vaciago & Coulson, 1975).

Molecular conformation

The conformation of the molecule is described by its torsion angles which are listed in Table 4. The conformation within the succinate group along the sequence C(1)—O(2)—C(7)—C(8)—C(8′)—C(7′)—O(2′)—C(1′) is all *trans*. However, the C(2)—C(1)—O(2)—C(7) torsion angle is 116·0° making the conformation

Table 3. *Comparison of bond distances (Å), bond angles (°) and torsion angles (°) of compounds related to diphenyl succinate*

	CH_2–CH_2	X–CH_2–CH_2	CH_2–CH_2–Y	X–CH_2CH_2–Y	Reference
HOOC–CH_2–CH_2–COOH(β)	1·50 (2)	112		T*	Morrison & Robertson (1949)
HOOC–CH_2–CH_2–COOH(β)	1·533 (19)	113·1		T	Broadley, Cruickshank, Morrison, Robertson & Shearer (1959)
HOOC–CH_2–CH_2–COOH–benzamide	1·528 (5)	112·7 (3)		T	Huang, Leiserowitz & Schmidt (1973)
HOOC–CH_2–CH_2–$COO^-.Cs^+$	1·52 (5)†	118 (3)†		T	McAdam & Speakman (1971)
HOOC–CH_2–CH_2–$COO^-.K^+$	1·510 (5)	114·3 (2)		T	McAdam, Curie & Speakman (1971)
	1·524 (6)‡	115·2 (8)‡			
^-OOC–CH_2–CH_2–$COO^-.2Li^+$	1·525 (2)	109·5 (1)		T	Klapper & Küppers (1973)
^-OOC–CH_2–CH_2–$COO^-.Cu^{2+}$	1·508 (13)	113·2 (11)	113·9 (11)	C	O'Connor & Maslen (1966)
H_2NOC–CH_2–CH_2–$CONH_2$	1·501 (3)	113		T	Davis & Pasternak (1956)
H_5C_6–OOC–CH_2–CH_2–COO–C_6H_5	1·507 (6)	111·8 (3)		T	This work
–O–CH_2–CH_2–O–	1·499 (3)	104·7 (2)	105·2 (2)	T	Pérez & Brisse (1976)
–O–CH_2–CH_2–O–	1·493 (3)	107·3 (2)		G	Pérez & Brisse (1975)
–O–CH_2–CH_2–NH^+–	1·506 (8)	108·0 (12)	115·6 (12)†	G	Griffith & Robertson (1972)
–O–CH_2–CH_2–CH_3	1·460 (5)	108·8 (3)	111·1 (3)†	T	Nakanishi & Ueno (1976)
H_2N–CH_2–CH_2–CH_3	1·545 (19)†	113·1 (13)†	115·4 (10)†	G	Tranqui, Vicat, Thomas, Pera, Fillion & Luu Duc (1976)
–S–CH_2–CH_2–Cl	1·501 (4)	111·6 (3)	110·8 (3)	T	Glusker & Zacharias (1972)
–S–CH_2–CH_2–Cl	1·478 (5)	110·0 (3)	109·5 (3)	T	Lewis, Carrell, Glusker & Sparks (1976)

* Torsion angles: $T \sim 180°$, $G \sim \pm 60°$, $C \sim 0°$.
† Not used in the average.
‡ Neutron diffraction data.

Table 4. *Torsion angles* (°)

The primed atoms are centrosymmetrically related to the unprimed atoms having the same number.

C(1)–O(2)–C(7)–C(8)	176·8 (3)	C(2)–C(1)–O(2)–C(7)	116·0 (3)
O(2)–C(7)–C(8)–C(8′)	174·8 (3)	C(6)–C(1)–O(2)–C(7)	−67·5 (4)
C(7)–C(8)–C(8′)–C(7′)	180·0		

of this part of the molecule *gauche*. A very similar situation was found in the structure of phenyl benzoate where the dihedral angle between the carboxylic and phenyl groups was 65·1° (Adams & Morsi, 1976). In our case the dihedral angle between the aromatic mean plane [C(1) to C(6)] and the succinate group [O(1), O(2), C(7), C(8) and the center of symmetry] is 67·7°. The conformation of diphenyl succinate can also be compared with that found in the structure of poly(*p*-phenylene oxide): $[O–C_6H_4]_n$ (Boon & Magré, 1969). In this structure it was found that the chain was made up of linear O–C_6H_4 elements. The potential-energy curves computed for the rotation of the phenylene group about the O–C_6H_4–O axis of a zigzag chain, with a bond angle of 124° at the O atoms, show a minimum at ±40° from the planar conformation. The structure proposed for poly(*p*-phenylene oxide) was achieved by alternating rotations of 50°, in good agreement with the calculation. Similarly, the conformation found in this work for rotation around the C_6H_4–O– bond falls in the allowed energy region for a C(1)–O(2)–C(7) bond angle of 118·4°.

Using the concept of the model compound (Brisse, Pérez & Marchessault, 1979) one can predict that the fiber repeat of the related polymer, poly(*p*-phenylene succinate), $[C_6H_4O–CO–(CH_2)_2–CO–O]_n$, would be close to 11·09 Å (Fig. 1). Although this polymer has been reported to be crystalline (Edgar & Hill, 1952), no value for its fiber repeat has yet been published. All the intermolecular distances are longer than the sum of the corresponding van der Waals radii; consequently the molecules are held in the crystal by van der Waals forces only.

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The Crystal Structures of Two Modifications of 3,5-Dinitro-L-tyrosine

BY VIVIAN CODY,* DAVID A. LANGS AND JOHN P. HAZEL

Medical Foundation of Buffalo, Inc., 73 *High Street, Buffalo, New York* 14203, *USA*

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Abstract

The crystal and molecular structure of 3,5-dinitro-L-tyrosine (DNT) has been determined in two crystalline modifications. Crystal (I), diaquasodium 3,5-dinitro-L-tyrosinate monohydrate $[C_9H_8N_3O_7^-.(H_2O)_2\text{-}Na^+.H_2O]$ has a triclinic lattice, $P1$, $Z = 2$, $a = 8{\cdot}271\,(3)$, $b = 13{\cdot}357\,(5)$, $c = 6{\cdot}864\,(2)$ Å, $\alpha = 110{\cdot}4\,(3)$, $\beta = 97{\cdot}0\,(2)$, and $\gamma = 92{\cdot}7\,(3)°$; crystal (II), 3,5-dinitro-L-tyrosine monohydrate $(C_9H_9N_3O_7.H_2O)$, has an orthorhombic lattice, $P2_12_12_1$, $Z = 4$, $a = 7{\cdot}8877\,(3)$, $b = 20{\cdot}1926\,(6)$ and $c = 7{\cdot}4242\,(3)$ Å. The two dinitro-L-tyrosine molecules in crystal (I) differ primarily in their amino acid conformations; one [(I*B*)] has the carbonyl group extended, while in the other [(I*A*)] it is folded back over the ring. The conformation in crystal (II) has the carbonyl group extended, similar to that of one of the forms observed in crystal (I). The nitrate groups are nearly coplanar with their respective rings in crystal (I), while they deviate more significantly from coplanarity in crystal (II). The phenolic bonds in the two DNT molecules in crystal (I) are significantly different from each other (1·298/1·234 Å); that in molecule (I*A*) is a hydroxyl with an intramolecular hydrogen bond and that in (I*B*) is a phenoxide ion. The phenolic bond in crystal (II) (1·306 Å) has the same geometry as that in (I*A*) but has no intramolecular hydrogen bond. The sodium ions in

* To whom correspondence should be addressed.

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