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## Dinitrobenzoate Derivative of a Chiral Arylcyclopentane

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### Abstract

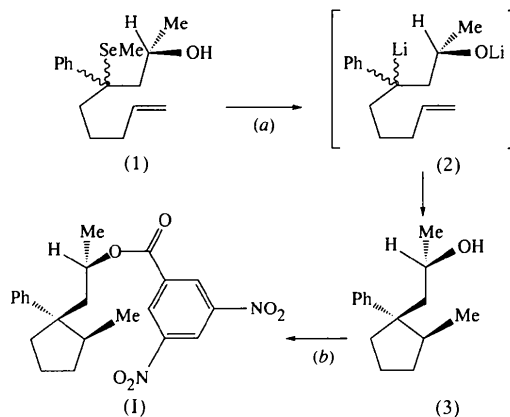
The structure of (2*S*)-1-[(1*S*,2*R*)-2-methyl-1-phenylcyclopentyl]-2-propyl 3,5-dinitrobenzoate, C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub>, (I), has been determined and the observed conformation is discussed. The observed proximity of the phenyl and dinitrobenzoate moieties can be explained by intramolecular electrostatic forces. Compound (I) was synthesized by carbocyclization followed by acylation with 3,5-dinitrobenzoyl chloride.

### Comment

$\omega$ -Alkenylbenzylolithiums, readily available from the corresponding selenides and butyllithium, possess a very high propensity to cyclize in cyclopentyl-methyl-lithiums and to produce, after hydrolysis, 1-phenyl-2-methylcyclopentanes in high yield (Krief & Barbeaux, 1987). The control of the relative stereochemistry is very high; the cyclopentyl derivative possessing *cis* stereochemistry between the phenyl and methyl groups is obtained when the reaction is carried out in alkanes or in ether, whereas the *trans* stereoisomer is obtained in tetrahydrofuran. We have, therefore, studied the asymmetric version of this reaction (Krief & Bousbaa, 1996).

We have performed the carbocyclization reaction on the organolithium derivative (2) bearing a remote chi-

ral centre in a suitable position to promote diastereofacial differentiation. Using proper reaction conditions (reaction *a*), we were able to obtain compound (3) in high yield (90%) and in high diastereoisomeric ratio (82%). To establish unambiguously the stereochemistry of this major reaction product, the three-dimensional structure of its 3,5-dinitrobenzoate derivative, (I), obtained by reaction (*b*), was determined by single-crystal X-ray diffraction.



- (a) (i) 1.1 eq. MeLi–LiBr–ether, 293 K, 5 min;  
 (ii) 1.1 eq. *tert*-BuLi–pentane, ether, 253 K, 1 h;  
 (iii) MeOH, 253 K;  
 (b) Cl(CO)Ph(NO<sub>2</sub>)<sub>2</sub>, DMAP, pyridine, 298 K, 1 h.

The configuration of compound (I) (Fig. 1) is 1*S*,2*R*,7*S* because the stereochemistry of the C7 atom is known to be *S*. Indeed, compound (I) was derived from the enantiomerically pure compound (1), itself synthesized using 2(*S*)-propylene oxide (Krief & Bousbaa, 1996). The thermal agitation parameters of the carbonyl O2 atom and the atoms of the nitro groups (N1, N2, O3–O6) are very high; this situation is discussed in the *Experimental* section. The five-membered ring (C1–C5) is in an ‘envelope’ conformation, with the C2 atom pointing out of the plane defined by the four other atoms. However, the characteristic sequence of values of the corresponding torsion angles ( $\omega_1, -\omega_1, \omega_2, 0, -\omega_2$ ; Dunitz, 1979) is only fairly well observed (Table 1). In particular, there is a difference of 13° between the absolute values of torsion angles C2–C3–C4–C5 and C2–C1–C5–C4. This could be the result of steric interactions between the C6 and C15 atoms, linked in *cis* positions relative to the adjacent C1 and C2 atoms, respectively.

Despite the flexibility of the chain of atoms C1–C6–C7–O1, the phenyl and dinitrobenzoate substituents are close to each other; the distance between the centroids of the rings is 4.88 Å and the planes defined by the two cycles form an angle of 55.96(13) Å [this situation imposes a ‘*gauche*’ conformation on the C9–C1–C6–C7 and C1–C6–C7–O1 chains

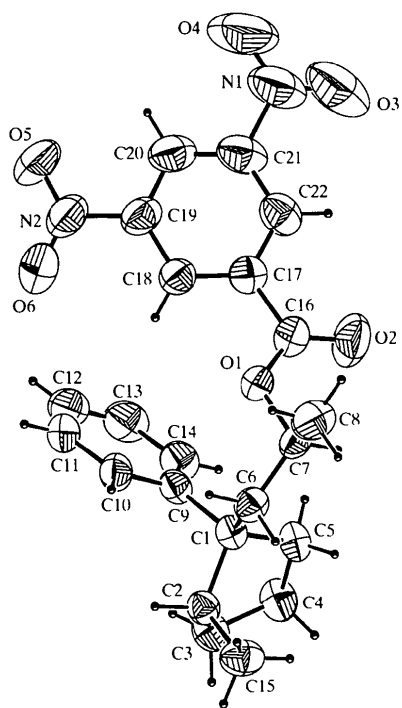


Fig. 1. The molecular structure of compound (I). Displacement ellipsoids are drawn at the 50% probability level.

(Table 1)]. Examination of the crystal packing revealed no specific intermolecular interactions that could explain this state. Searching for equivalent situations (a dinitrobenzoate and a phenyl group linked by a chain of three C atoms, whose C—C bonds are not in rings) in the Cambridge Structural Database (CSD Version 5.14 of October 1997; Allen & Kennard, 1993), we found only two compounds (BIYNOM and MHPNBZ10) with a similar connectivity but with very different conformations. In the case of BIYNOM, the phenyl and dinitrobenzoate groups of two different molecules are in relative positions somewhat similar to the situation observed for compound (I). The distance between the centroids of the rings is 5.33 Å. Interestingly, in BIYNOM, two H atoms of the phenyl substituent are directed toward the plane of the dinitrobenzoate group, in contrast to compound (I), where only one H atom (H18) of the dinitrobenzoate points toward the plane defined by the phenyl substituent.

The observed proximity of the two aromatic rings of compound (I) can be understood, to a large extent, by electrostatic intramolecular forces. It is well known that the phenyl substituent behaves, electrostatically, like a quadrupole (Williams, 1993; Luhmer *et al.*, 1994). On the other side, the dinitrobenzoate group is like a dipole; the phenyl ring is polarized by the nitro and carboxylate functions. So, coulomb attraction forces between the quadrupole and the dipole can explain the position of the two substituents discussed.

## Experimental

Details of the synthesis of compound (3) have been described elsewhere (Krief & Bousbaa, 1996). For the synthesis of compound (I), compound (3) (6.15 mmol, 1.34 g,  $M_r = 218$ ) and 4-(dimethylamino)pyridine (DMAP; 0.615 mmol, 75 mg,  $M_r = 122$ ) dissolved in pyridine (7 ml, distilled over KOH) were placed under argon in a 100 ml two-necked flask equipped with a magnetic stirrer. 3,5-Dinitrobenzoyl chloride (7.38 mmol, 1.7 g) was added in fractions. The reaction mixture became warm, turned brown and a precipitate appeared. The reaction was followed by thin-layer chromatography (diethyl ether/pentane eluent, 4:6 v/v). After 1 h of reaction at room temperature, compound (3) had disappeared and the reaction mixture was dissolved in diethyl ether, washed first with water, then three times with a 10% aqueous solution of HCl, and finally three times with water, to obtain a neutral pH. The organic phase was dried over MgSO<sub>4</sub> and the solvents evaporated under reduced pressure. The 2.05 g of crude product obtained was fractionated on an SiO<sub>2</sub> column (diethyl ether/pentane eluent, 1:9 v/v) and 1.960 g (77% yield) of product was obtained ( $R_f = 0.28$ ). This product was dissolved in a minimum of diethyl ether, and pentane was added until the solution became cloudy. The resulting mixture was cooled at 253 K for 5 h. The crystals obtained were filtered, washed with pentane, dried and recrystallized by the same method to obtain finally 853 mg of compound (I) [ $M_r = 412.45$ ; m.p. 363–364 K;  $[\alpha]_D^{20} = 212.3$  (2 g/100 ml CHCl<sub>3</sub>); analysis: C 63.71, H 5.87, N 6.65%; C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub> requires: C 64.06, H 5.85, N 6.79%].

### Crystal data

C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub>  
 $M_r = 412.43$   
 Monoclinic  
*P*2<sub>1</sub>  
 $a = 6.189$  (1) Å  
 $b = 10.614$  (1) Å  
 $c = 16.160$  (1) Å  
 $\beta = 100.993$  (4)°  
 $V = 1042.1$  (2) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.314$  Mg m<sup>-3</sup>  
 $D_m$  not measured

### Data collection

Enraf–Nonius CAD-4  
 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: none  
 3384 measured reflections  
 2937 independent reflections  
 2847 reflections with  
 $I > 2\sigma(I)$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.116$   
 $S = 1.092$

Cu  $K\alpha$  radiation  
 $\lambda = 1.54178$  Å  
 Cell parameters from 25  
 reflections  
 $\theta = 40$ – $50^\circ$   
 $\mu = 0.799$  mm<sup>-1</sup>  
 $T = 292$  (2) K  
 Irregular shape  
 0.20 × 0.15 × 0.10 mm  
 Transparent, colourless

$R_{int} = 0.017$   
 $\theta_{max} = 72.01^\circ$   
 $h = 0 \rightarrow 7$   
 $k = -9 \rightarrow 13$   
 $l = -19 \rightarrow 19$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 2.0%

$(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.159$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.229$  e Å<sup>-3</sup>  
 Extinction correction: none

2937 reflections  
271 parameters  
H atoms constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0746P)^2 + 0.0914P]$   
where  $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from  
*International Tables for  
Crystallography* (Vol. C)  
Absolute structure: Flack  
(1983)  
Flack parameter = 0.0 (3)

Table 1. Selected torsion angles ( $^\circ$ )

C5—C1—C2—C3	-42.8 (2)	C2—C1—C5—C4	31.6 (2)
C1—C2—C3—C4	38.5 (2)	C9—C1—C6—C7	-75.6 (2)
C2—C3—C4—C5	-18.6 (2)	C1—C6—C7—O1	63.7 (2)
C3—C4—C5—C1	-8.7 (2)		

The thermal agitation parameters of the carbonyl O2 atom have important values that could be considered as abnormal. But the carbonyl C16 atom directly connected to O2 is considerably less agitated. So, these large values are the image of an important out-of-plane bending and it is not necessary to introduce atomic sites with fractional occupancy. Atoms O3—O6 of the two nitro groups are also considerably agitated. This seems to be the combined result of rotational movements of these nitro groups around their C—N axes coupled with large translational movements resulting from their terminal position in the molecule. Here also, it is not necessary to introduce atomic sites with fractional occupancy.

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1992). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *NONIUS93* (Baudoux & Evrard, 1993). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1180). Services for accessing these data are described at the back of the journal.

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## 2-Methoxy-3-methyl-6-[(triphenylphosphoranylidene)amino]pyrimidin-4(3*H*)-one and 3-Methyl-2-methylthio-6-[(triphenylphosphoranylidene)amino]pyrimidin-4(3*H*)-one

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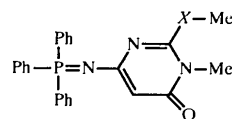
(Received 17 February 1998; accepted 5 March 1998)

## Abstract

Structure analyses of the 2-methoxy- [C<sub>24</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub>P, (1)] and 2-methylthio- [C<sub>24</sub>H<sub>22</sub>N<sub>3</sub>OPS, (2)] title compounds show that while they are not isomorphous, they do have very similar conformations in the solid state. In both compounds, there are deviations from ideal tetrahedral symmetry around the P atoms, *e.g.* the N—P—C angles are in the range 105.57 (9)–117.81 (9) $^\circ$  in (1) and 105.75 (12)–118.22 (13) $^\circ$  in (2). This is consistent with the behaviour of the methyl-group signals in their NMR spectra.

## Comment

The title compounds, (1) and (2), and related compounds have been used as intermediates in several reactions in which the triphenylphosphoranylidene group is used to protect an amino group from unwanted reactions (Wamhoff & Schupp, 1986; Wamhoff *et al.*, 1986). The X-ray analyses of (1) and (2) were undertaken to establish the solid-state conformations and correlate these with NMR spectral data.



- (1) X = O  
(2) X = S

Views of (1) and (2) are presented in Figs. 1 and 2, respectively; the compounds are not isomorphous, but they are isostructural. The methoxy group in (1) and the