CRYSTALLOGRAPHIC
COMMUNICATIONS

ISSN 2056-9890

Crystal structure of *r*-1,*c*-2-dibenzoyl-*t*-3,*t*-4-bis(2-nitrophenyl)cyclobutane

Manuel Velasco Ximello,[a] Sylvain Bernès,[b] Aarón Pérez-Benítez,[c] Ulises Hernández Pareja,[a] Angel Mendoza,[a] Jorge R. Juárez Posadas[a] and Jaime Vázquez Bravo[d]*

[a]Centro de Química, Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla, Edif. IC8 Complejo de Ciencias, C.U., 72570 Puebla, Pue., Mexico, [b]Instituto de Física, Benemérita Universidad Autónoma de Puebla, Av. San Claudio y 18 Sur, 72570 Puebla, Pue., Mexico, [c]Facultad de Ciencias Químicas, Benemérita Universidad Autónoma de Puebla, Av. San Claudio y 18 Sur, 72570 Puebla, Pue., Mexico, and [d]Ingeniería en Biotecnología, Universidad Politécnica Metropolitana de Puebla, Popocatépetl s/n, Tres Cerritos, 72480 Puebla, Pue., Mexico. *Correspondence e-mail: jaime.vazquez@metropoli.edu.mx

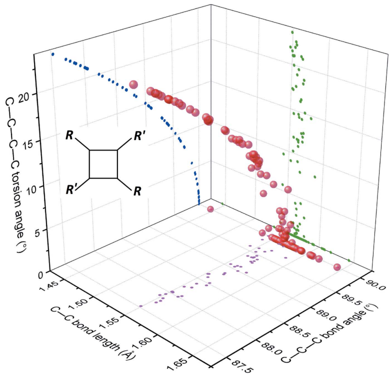
Received 14 October 2017
Accepted 1 November 2017

Edited by J. Ellena, Universidade de Sâo Paulo, Brazil

Keywords: crystal structure; cyclobutane; truxillic isomer; truxinic isomer; chalcone.

CCDC reference: 1583527

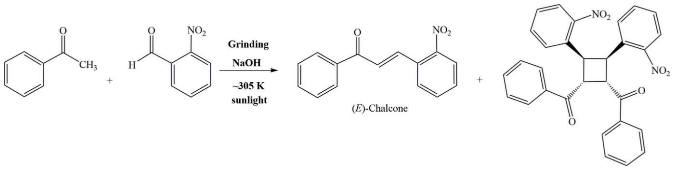
Supporting information: this article has supporting information at journals.iucr.org/e



The condensation reaction of acetophenone (1-phenylethan-1-one) with 2-nitrobenzaldehyde in the molten state yielded the expected chalcone, (*E*)-3-(2-nitrophenyl)-1-phenylprop-2-en-1-one, and, unexpectedly, the title compound, $C_{30}H_{22}N_2O_6$, which results from the *syn* head-to-head [2 + 2] cycloaddition of the chalcone. The molecular structure of the dimer shows that the four benzene rings of the substituents are oriented in such a way that potential steric hindrance is minimized, whilst allowing some degree of intermolecular π–π interactions for crystal stabilization. In the molecule, one nitro group is disordered over two positions, with occupancies for each part of 0.876 (7) and 0.127 (7).

1. Chemical context

The [2 + 2]-photocycloaddition reaction is the most frequently used photochemical reaction to access four-membered carbon rings. An emblematic application of this large class of reactions is the synthesis of cage compounds such as cubane (Eaton & Cole, 1964). On the other hand, [2 + 2] cycloaddition may be also a key tool for the synthesis of some natural compounds including a functionalized cyclobutane ring, for example sceptrin, isolated from a marine sponge (Ma *et al.*, 2014), ediandrin, isolated from the roots of an Australian rainforest plant (Davis *et al.*, 2009), or incarvillateine, isolated from the aerial parts of a wild plant found in China (Nakamura *et al.*, 1999; Ichikawa *et al.*, 2004).



The syntheses of these compounds generally involves photochemical dimerization of olefins, α,β-unsaturated carbonyl, or carboxyl compounds. Traditionally, these compounds have been synthesized through intermolecular [2 + 2]-photocycloaddition reaction of 1,3-diarylprop-2-en-1-ones (also known as chalcones) in solution (Kumar *et al.*, 2017), or in the solid state and molten state, under UV irradiation. The cycloaddition of (*E*)-chalcones may give four

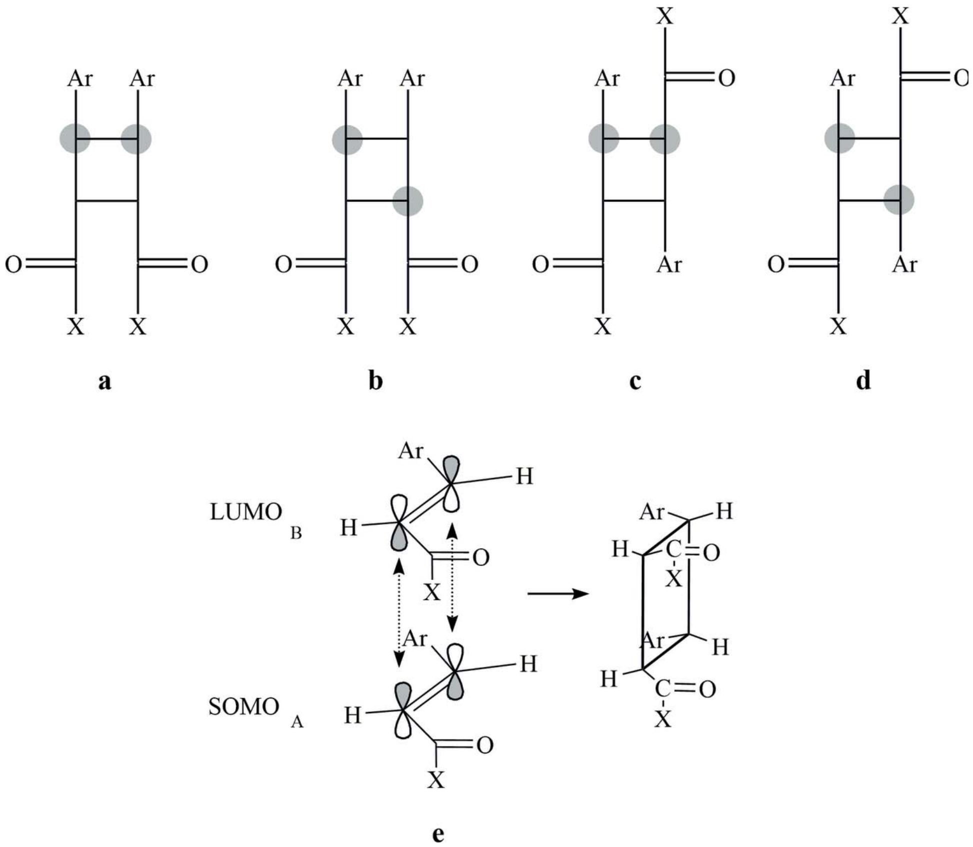


Figure 1
The four possible stereoisomers resulting from the [2 + 2]-cycloaddition of (*E*)-chalcones (Cibin *et al.*, 2003): (*a*) *syn* head-to-head; (*b*) *anti* head-to-head; (*c*) *syn* head-to-tail and (*d*) *anti* head-to-tail; (*e*) *supra–supra* bonding interaction (π^2s + π^2s) of SOMO–LUMO to produce the *syn* head-to-head stereoisomer shown in (*a*).

possible stereoisomers, namely *syn*/*anti*, head-to-head and head-to-tail (Fig. 1), depending on the physical state of the substrate (solid, solution or molten state) and on other reaction conditions, such as the type of glassware used for the workup.

Herein we report the synthesis and structure of a new chalcone dimer, obtained fortuitously while preparing the monomeric chalcone (see *Scheme*). The title compound corresponds to the *syn* head-to-head stereoisomer (Fig. 1*a*), which could arise from a *supra–supra* bonding interaction between the singly occupied molecular orbital (SOMO) of one chalcone and the lowest unoccupied molecular orbital (LUMO) of the other one (Fig. 1*e*; Smith, 2016). Since we detected only one stereoisomer corresponding to the cycloaddition product in the mixture of the reaction carried out under sunlight, we assume that dimerization is actually performed *via* this mechanism. Indeed, the proposed mechanism is consistent with the structure reported herein.

2. Structural commentary

The topochemical solid-state dimerization of the chalcone (*E*)-3-(2-nitrophenyl)-1-phenylprop-2-en-1-one resulted in the title tetrasubstituted cyclobutane derivative (Fig. 2). The *rctt* (*cis*, *trans*, *trans*) relative stereochemistry of the substituents is identical to that of β-truxinic acid, obtained by photodimerization of cinnamic acid (Hein, 2006), indicating that dimerization occurred *via* a *syn* head-to-head [2 + 2] cycloaddition of the chalcone.

The molecule potentially belongs to the C_s point group, but crystallizes in a general position in space group $P\overline{1}$. The cyclobutane ring is thus non-planar, unlike many head-to-tail photodimerizations adducts, which crystallize with the ring placed about an inversion centre (see *Database survey* section). However, the departure from planarity is very small, the dihedral angle between the C1/C2/C3 and C1/C4/C3 mean planes being 3.6 (2)°. Some other *rctt* tetrasubstituted cyclobutane derivatives have a more marked butterfly conformation, which apparently results from steric restrictions imposed by bulky substituents (*e.g.* Strabler *et al.*, 2013). In the case of the title compound, the *cis* benzoyl and nitrobenzene groups are oriented

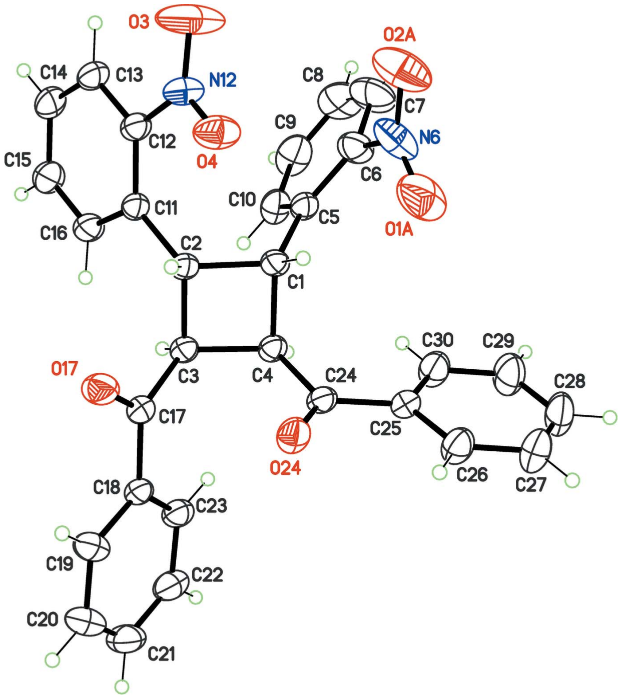


Figure 2
Molecular structure of the title cyclobutane, with displacement ellipsoids at the 30% probability level for non-H atoms. Disordered atoms O1*B* and O2*B* have been omitted.

in such a way that intramolecular π–π or C—H$\cdots\pi$ contacts are avoided. The shortest centroid-to-centroid separation is larger than 4.2 Å, for the nitrobenzene rings, which form a dihedral angle of 45.73 (8)°. In contrast, an intermolecular π–π contact is formed by parallel C11–C16 mnitobenzene rings related by an inversion centre. In that case, the separation between the rings is 3.883 (1) Å. These features seem to indicate that the molecular conformation is optimized in order to avoid steric hindrance, whilst at the same time allowing an efficient packing for the crystal stabilization.

The geometry of the cyclobutane ring matches the statistics computed by *MOGUL* (Bruno *et al.*, 2004). The C—C bond lengths range from 1.542 (2) to 1.580 (3) Å and the C—C—C angles range from 88.90 (13) to 90.76 (13)° (*MOGUL* medians: m = 1.558–1.565 Å and m = 88.7–89.5°, respectively). On the other hand, the average of absolute values for torsion angle defined by the four C atoms of the cyclobutane ring is $\langle|\delta|\rangle$ = 2.52 (2)°. All these features support the conclusion reached by another research group who determined the structure of a closely related compound, namely a cyclobutane substituted by two benzoyl and two methoxyphenyl groups (Steyl *et al.*, 2005): the total distortion of the cyclobutane ring increases while additional functionalization of the benzene rings is achieved, due mainly to steric effects. In that sense, the title molecule belongs to the class of cyclobutane derivatives exhibiting almost no puckering distortion.

3. Database survey

A survey of the current organic sub-set of the CSD database (CSD 5.38 updated May 2017; Groom *et al.*, 2016) was performed for cyclobutane derivatives formulated $C_4H_4R_2R'_2$ where R and R' are two different substituents. The data set was limited to cyclobutanes for which each C atom is substituted by exactly one H atom and one non-H substituent, and all hits for which the cyclobutane is fused with one or various cyclic systems were omitted. The resulting hits for which 3D coordinates are available were checked by hand in order to eliminate cyclobutanes substituted by three or four different substituents and those for which the four substituents are identical. Finally, structures determined several times were filtered to avoid statistical bias, and some severely disordered cases unsuitable for geometric computations were also deleted. The final working set contained 225 cyclobutanes $C_4H_4R_2R'_2$ comparable with the title compound (see deposited *Excel* file).

Within this set, 77% of the cyclobutanes result formally from a head-to-tail dimerization (known as truxillic type), many of them (108) with the cyclobutane lying on a special position. The remaining 23% result formally from a head-to-head dimerization (known as truxinic type), and only one of them displays crystallographic symmetry (cyclobutane of sceptrin, placed on a twofold axis in space group $C2$; Ma *et al.*, 2014). Although the truxillic cyclobutanes thus have a marked tendency to be more 'symmetric' than the truxinic co-set, both groups are very similar regarding their conformational flexibility. The range of distortion accessible for the cyclobutane

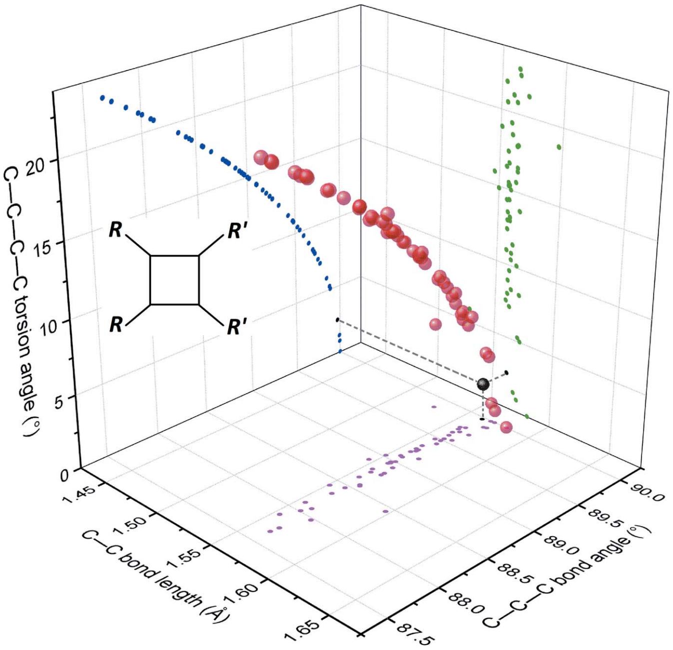


Figure 3
A plot of the geometric parameters for truxinic-type cyclobutanes with formula $C_4H_4R_2R'_2$ retrieved from the CSD. Each red ball corresponds to one cyclobutane ring in the three-dimensional space defined by the average of four bond lengths, the average of four bond angles, and the average of the absolute values of the four torsion angles in the cycle. This distribution is also projected on three two-dimensional spaces, for each couple of geometric parameters (magenta, green, and blue dots). The parameters for the title compound are represented with black dots.

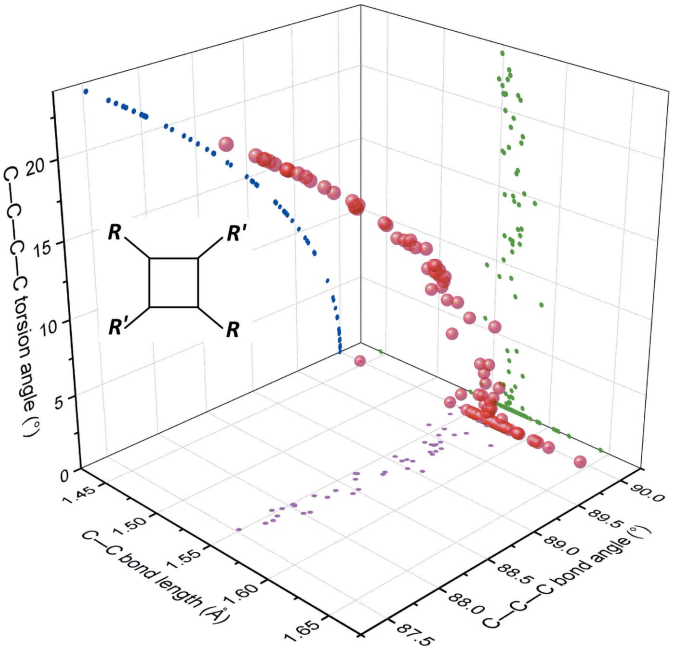


Figure 4
A plot similar to that of Fig. 3, for truxillic-type cyclobutanes with formula $C_4H_4R_2R'_2$ retrieved from the CSD. The same scale for the three axis of the space is used in both figures, for comparison purposes. Note the cluster of points with the averages of bond angles constrained to 90°, corresponding to cyclobutanes planar by symmetry.

ring may be estimated by plotting the geometric parameters describing the conformation of the ring: bond lengths, angles, and torsion angles (Figs. 3 and 4). The distributions observed for 52 truxinic cyclobutanes (Fig. 3) and 174 truxillic cyclobutanes (Fig. 4) are almost identical, with the exception of the accumulation of data at bond angles of 90° in the latter, due to the occurrence of rings planar by symmetry. The same applies to the distortion of the rings in both groups, for example, for the functions $\tau = \tau(\theta)$, where θ is a bond angle and τ a torsion angle (blue curves in Figs. 3 and 4). Indeed, these distributions are perfectly fitted using the same power function in both groups: $\tau = 15(\theta - 90)^{0.5}$, where τ and θ are expressed in degrees.

The title compound belongs to the truxinic group, and exhibits a very small distortion for the cyclobutane ring, compared to other truxinic derivatives (see black dots in Fig. 3). Only three other related truxinic derivatives for which the X-ray structures have been published present a more planar cyclobutane ring. It thus appears that the substituents in the title molecule, benzoyl and 2-nitrophenyl, have very little steric influence on the central ring.

4. Synthesis and crystallization

A mixture of acetophenone (0.52 g, 4.38 mmol), 2-nitrobenzaldehyde (0.66 g, 4.38 mmol) and solid NaOH pellets (0.17 g, 4.38 mmol) were ground in an agate mortar with a pestle, at room temperature, for 23 min. The reaction proceeds exothermically (as noted by a rise in temperature of about 5–12 K). The progress of the reaction was monitored by TLC. After completion, the mixture was diluted with CH_2Cl_2 and washed with brine. The organic layer was separated, dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography using silica-gel and hexanes–ethyl acetate 4:1 as eluent, to give the expected chalcone and the title compound (0.66 g, 30%), as brown and colourless solids, respectively. Cyclobutane derivative: m.p. 517 K. FT–IR ν_{max}/cm^{-1} 1659 (C═O), 1557, 1348 (NO_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm: 7.81–7.33 (18H, *m*, ArH), 5.22 (2H, *m*, CH) and 4.87 (2H, *m*, CH). ^{13}C NMR (125 MHz, $CDCl_3$) δ/ppm: 44.3, 46.8, 125.0, 128.3, 129.4, 129.6, 130.4, 133.1, 134.7, 136.7, 137.5, 148.6, 196.9. HRMS (EI) calculated for $C_{30}H_{22}N_2O_6$ (M^+) 506.1478; found 506.1477.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. One of the nitro groups is disordered by rotation about its C—NO_2 bond, and was refined with two parts for the O atoms: O1*A*/O2*A* with occupancy 0.876 (7) and O1*B*/O2*B* with occupancy 0.124 (7). These four sites were restrained to have similar displacement parameters, with standard deviation of 0.04 Å^2. The same restriction was applied to the O atoms of the other nitro group, O3/O4, given that this nitro group is probably also affected by disorder, although we were unable to refine a suitable model on the basis of the room temperature data for this group. The C-bound H atoms were treated as riding atoms in geometrically idealized positions: C—H 0.93–0.98 Å with U_{iso}(H) = 1.2U_{eq}(C).

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{30}H_{22}N_2O_6$
M_r	506.49
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	295
a, *b*, *c* (Å)	7.2599 (5), 10.5614 (5), 16.7351 (8)
α, β, γ (°)	78.863 (4), 87.472 (5), 85.238 (5)
V (Å^3)	1254.13 (13)
Z	2
Radiation type	Mo *Kα*
μ (mm^{-1})	0.10
Crystal size (mm)	0.37 × 0.20 × 0.15
Data collection	
Diffractometer	Agilent Xcalibur Atlas Gemini
Absorption correction	Analytical (*CrysAlis PRO*; Agilent, 2013)
T_{min}, T_{max}	0.962, 0.983
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25649, 5116, 3292
R_{int}	0.051
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.053, 0.164, 1.04
No. of reflections	5116
No. of parameters	363
No. of restraints	24
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.27

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*), *XP* in *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008).

Funding information

We are grateful to VIEP–BUAP for financial support. MVX and UHP thank CONACyT for their scholarships (297948 and 277416), project CONACyT 173585 and PRODEP UPMP-PTC-007.

References

Agilent (2013). *CrysAlis PRO*, Agilent Technologies Inc., Santa Clara, CA, USA.

Bruno, I. J., Cole, J. C., Kessler, M., Luo, J., Motherwell, W. D. S., Purkis, L. H., Smith, B. R., Taylor, R., Cooper, R. I., Harris, S. E. & Orpen, A. G. (2004). *J. Chem. Inf. Comput. Sci.* **44**, 2133–2144.

Cibin, F. R., Doddi, G. & Mencarelli, P. (2003). *Tetrahedron*, **59**, 3455–3459.

Davis, R. A., Barnes, E. C., Longden, J., Avery, V. M. & Healy, P. C. (2009). *Bioorg. Med. Chem.* **17**, 1387–1392.

Eaton, P. E. & Cole, T. W. (1964). *J. Am. Chem. Soc.* **86**, 3157–3158.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Hein, S. M. (2006). *J. Chem. Educ.* **83**, 940–942.

Ichikawa, M., Takahashi, M., Aoyagi, S. & Kibayashi, C. (2004). *J. Am. Chem. Soc.* **126**, 16553–16558.

Kumar, S., Salian, V. V., Narayana, B., Sarojini, B. K., Anthal, S. & Kant, R. (2017). *Rasayan J. Chem.* **10**, 522–527.

Ma, Z., Wang, X., Wang, X., Rodriguez, R. A., Moore, C. E., Gao, S., Tan, X., Ma, Y., Rheingold, A. L., Baran, P. S. & Chen, C. (2014). *Science*, **346**, 219–224.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Nakamura, M., Chi, Y. M., Yan, W. M., Nakasugi, Y., Yoshizawa, T., Irino, N., Hashimoto, F., Kinjo, J., Nohara, T. & Sakurada, S. (1999). *J. Nat. Prod.* **62**, 1293–1294.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Smith, M. (2016). *Organic Synthesis*, 4th edition. Academic Press.

Steyl, G., Hill, T. & Roodt, A. (2005). *Acta Cryst.* E**61**, o1978–o1980.

Strabler, C., Ortner, T., Prock, J., Granja, A., Gutmann, R., Kopacka, H., Müller, T. & Brüggeller, P. (2013). *Eur. J. Inorg. Chem.* pp. 5121–5132.

supporting information

Acta Cryst. (2017). E**73**, 1866-1870   [https://doi.org/10.1107/S2056989017015936]

Crystal structure of *r*-1,*c*-2-dibenzoyl-*t*-3,*t*-4-bis(2-nitrophenyl)cyclobutane

Manuel Velasco Ximello, Sylvain Bernès, Aarón Pérez-Benítez, Ulises Hernández Pareja, Angel Mendoza, Jorge R. Juárez Posadas and Jaime Vázquez Bravo

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008).

[3,4-Bis(2-nitrophenyl)cyclobutane-1,2-diyl]bis[(phenyl)methanone]

Crystal data

$C_{30}H_{22}N_2O_6$
$M_r = 506.49$
Triclinic, $P\overline{1}$
$a = 7.2599$ (5) Å
$b = 10.5614$ (5) Å
$c = 16.7351$ (8) Å
$\alpha = 78.863$ (4)°
$\beta = 87.472$ (5)°
$\gamma = 85.238$ (5)°
$V = 1254.13$ (13) Å^3
$Z = 2$

$F(000) = 528$
$D_x = 1.341$ Mg m^{-3}
Melting point: 517 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5272 reflections
$\theta = 3.6$–27.9°
$\mu = 0.10$ mm^{-1}
$T = 295$ K
Prism, colourless
0.37 × 0.20 × 0.15 mm

Data collection

Agilent Xcalibur Atlas Gemini diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 10.5564 pixels mm^{-1}
ω scans
Absorption correction: analytical (CrysAlis PRO; Agilent, 2013)
$T_{\min} = 0.962$, $T_{\max} = 0.983$

25649 measured reflections
5116 independent reflections
3292 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.051$
$\theta_{\max} = 26.4$°, $\theta_{\min} = 3.1$°
$h = -9 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.164$
$S = 1.04$
5116 reflections
363 parameters
24 restraints

0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0762P)^2 + 0.1873P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Extinction correction: SHELXL2016 (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.011 (3)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$	Occ. (<1)
C1	0.6552 (3)	0.64030 (16)	0.23390 (11)	0.0415 (4)	
H1A	0.548307	0.694892	0.209849	0.050*	
C2	0.6594 (3)	0.63982 (16)	0.32828 (11)	0.0406 (4)	
H2A	0.558141	0.699162	0.342918	0.049*	
C3	0.8388 (3)	0.71065 (17)	0.31510 (11)	0.0415 (4)	
H3A	0.942691	0.650434	0.336831	0.050*	
C4	0.8326 (3)	0.71816 (17)	0.22142 (11)	0.0414 (4)	
H4A	0.938656	0.668933	0.200920	0.050*	
C5	0.6680 (3)	0.51217 (17)	0.20721 (11)	0.0466 (5)	
C6	0.5325 (3)	0.4711 (2)	0.16339 (15)	0.0648 (6)	
C7	0.5406 (5)	0.3472 (3)	0.1475 (2)	0.0961 (10)	
H7A	0.447643	0.322545	0.118570	0.115*	
C8	0.6849 (5)	0.2614 (3)	0.1744 (2)	0.0980 (10)	
H8A	0.690019	0.177555	0.164369	0.118*	
C9	0.8229 (5)	0.2982 (2)	0.21645 (17)	0.0815 (8)	
H9A	0.922486	0.239823	0.234101	0.098*	
C10	0.8140 (3)	0.4216 (2)	0.23247 (13)	0.0591 (6)	
H10A	0.908604	0.445158	0.261050	0.071*	
C11	0.6561 (3)	0.51184 (17)	0.38742 (11)	0.0424 (4)	
C12	0.5073 (3)	0.43324 (18)	0.39869 (12)	0.0466 (5)	
C13	0.5125 (3)	0.3138 (2)	0.45159 (13)	0.0564 (6)	
H13A	0.410934	0.264323	0.456958	0.068*	
C14	0.6658 (4)	0.2693 (2)	0.49537 (13)	0.0637 (6)	
H14A	0.670172	0.189494	0.530677	0.076*	
C15	0.8138 (3)	0.3437 (2)	0.48669 (14)	0.0646 (6)	
H15A	0.919549	0.314127	0.516170	0.078*	
C16	0.8071 (3)	0.4627 (2)	0.43438 (13)	0.0565 (6)	
H16A	0.908810	0.511744	0.430641	0.068*	
C17	0.8343 (3)	0.83090 (18)	0.35266 (11)	0.0449 (5)	
C18	0.9976 (3)	0.91010 (17)	0.34225 (11)	0.0448 (5)	
C19	0.9958 (3)	1.0116 (2)	0.38363 (15)	0.0633 (6)	
H19A	0.892064	1.031224	0.414871	0.076*	
C20	1.1465 (4)	1.0838 (3)	0.37887 (18)	0.0789 (8)	
H20A	1.144193	1.151593	0.407100	0.095*	
C21	1.3000 (4)	1.0563 (3)	0.33276 (17)	0.0766 (8)	
H21A	1.401455	1.105457	0.329712	0.092*	
C22	1.3038 (3)	0.9565 (2)	0.29124 (15)	0.0642 (6)	
H22A	1.407992	0.937882	0.259970	0.077*	
C23	1.1527 (3)	0.8830 (2)	0.29563 (13)	0.0527 (5)	
H23A	1.155681	0.815337	0.267201	0.063*	

C24	0.7924 (3)	0.84768 (18)	0.16696 (12)	0.0438 (5)	
C25	0.8062 (3)	0.85576 (19)	0.07748 (12)	0.0469 (5)	
C26	0.7499 (3)	0.9703 (2)	0.02607 (14)	0.0623 (6)	
H26A	0.703596	1.041174	0.048177	0.075*	
C27	0.7615 (4)	0.9808 (3)	−0.05686 (15)	0.0782 (8)	
H27A	0.723599	1.058504	−0.090560	0.094*	
C28	0.8287 (4)	0.8769 (3)	−0.09014 (15)	0.0817 (8)	
H28A	0.836448	0.884338	−0.146453	0.098*	
C29	0.8843 (4)	0.7627 (3)	−0.04106 (15)	0.0809 (8)	
H29A	0.929398	0.692340	−0.063924	0.097*	
C30	0.8737 (4)	0.7515 (2)	0.04271 (14)	0.0647 (6)	
H30A	0.911977	0.673403	0.075957	0.078*	
N6	0.3729 (4)	0.5581 (3)	0.13166 (19)	0.0906 (8)	
O1A	0.3951 (6)	0.6676 (4)	0.1010 (3)	0.1231 (16)	0.876 (7)
O2A	0.2222 (4)	0.5095 (3)	0.1392 (2)	0.1287 (16)	0.876 (7)
O1B	0.307 (5)	0.642 (4)	0.154 (3)	0.149 (13)	0.124 (7)
O2B	0.360 (5)	0.567 (3)	0.0504 (17)	0.209 (16)	0.124 (7)
N12	0.3353 (2)	0.47251 (18)	0.35551 (12)	0.0607 (5)	
O3	0.2211 (3)	0.3957 (2)	0.3593 (2)	0.1493 (13)	
O4	0.3067 (2)	0.58039 (15)	0.31765 (11)	0.0740 (5)	
O17	0.7042 (2)	0.85530 (15)	0.39699 (10)	0.0658 (5)	
O24	0.7394 (2)	0.94134 (13)	0.19653 (9)	0.0615 (4)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0485 (11)	0.0308 (9)	0.0445 (10)	−0.0046 (8)	−0.0076 (8)	−0.0030 (8)
C2	0.0457 (10)	0.0316 (9)	0.0440 (10)	−0.0048 (8)	−0.0007 (8)	−0.0055 (8)
C3	0.0470 (10)	0.0339 (10)	0.0421 (10)	−0.0059 (8)	−0.0030 (8)	−0.0023 (8)
C4	0.0483 (11)	0.0326 (10)	0.0421 (10)	−0.0035 (8)	0.0017 (8)	−0.0049 (8)
C5	0.0628 (13)	0.0345 (10)	0.0422 (11)	−0.0086 (9)	0.0004 (9)	−0.0051 (8)
C6	0.0732 (16)	0.0551 (14)	0.0720 (15)	−0.0143 (12)	−0.0027 (12)	−0.0229 (12)
C7	0.113 (2)	0.0699 (19)	0.122 (3)	−0.0273 (18)	−0.004 (2)	−0.0510 (18)
C8	0.141 (3)	0.0449 (15)	0.117 (3)	−0.0163 (18)	0.019 (2)	−0.0380 (16)
C9	0.120 (2)	0.0465 (14)	0.0735 (17)	0.0141 (14)	0.0103 (16)	−0.0105 (12)
C10	0.0822 (16)	0.0420 (12)	0.0506 (12)	0.0059 (11)	−0.0009 (11)	−0.0074 (9)
C11	0.0531 (11)	0.0351 (10)	0.0397 (10)	−0.0077 (8)	0.0028 (8)	−0.0076 (8)
C12	0.0520 (12)	0.0402 (11)	0.0480 (11)	−0.0092 (9)	0.0055 (9)	−0.0082 (8)
C13	0.0727 (15)	0.0432 (12)	0.0525 (12)	−0.0185 (11)	0.0069 (11)	−0.0035 (9)
C14	0.0940 (18)	0.0417 (12)	0.0511 (13)	−0.0135 (12)	−0.0039 (12)	0.0056 (10)
C15	0.0793 (16)	0.0530 (13)	0.0561 (13)	−0.0101 (12)	−0.0166 (11)	0.0084 (10)
C16	0.0667 (14)	0.0472 (12)	0.0531 (12)	−0.0158 (10)	−0.0126 (10)	0.0037 (9)
C17	0.0540 (12)	0.0406 (11)	0.0396 (10)	−0.0094 (9)	−0.0002 (9)	−0.0045 (8)
C18	0.0523 (11)	0.0374 (10)	0.0425 (10)	−0.0107 (9)	−0.0059 (9)	0.0019 (8)
C19	0.0747 (15)	0.0518 (13)	0.0689 (15)	−0.0207 (11)	0.0016 (12)	−0.0192 (11)
C20	0.094 (2)	0.0624 (16)	0.0895 (19)	−0.0351 (14)	−0.0022 (16)	−0.0237 (14)
C21	0.0775 (18)	0.0671 (17)	0.0843 (18)	−0.0349 (14)	−0.0142 (14)	0.0031 (14)
C22	0.0563 (13)	0.0607 (15)	0.0687 (15)	−0.0143 (11)	−0.0032 (11)	0.0093 (12)

C23	0.0547 (12)	0.0450 (12)	0.0552 (12)	−0.0096 (10)	−0.0055 (10)	0.0022 (9)
C24	0.0495 (11)	0.0356 (10)	0.0455 (11)	−0.0080 (8)	0.0035 (8)	−0.0047 (8)
C25	0.0509 (11)	0.0442 (11)	0.0444 (11)	−0.0103 (9)	0.0007 (9)	−0.0029 (9)
C26	0.0765 (15)	0.0528 (13)	0.0530 (13)	0.0000 (11)	−0.0017 (11)	−0.0003 (10)
C27	0.0956 (19)	0.0791 (18)	0.0502 (14)	0.0041 (15)	−0.0057 (13)	0.0078 (13)
C28	0.106 (2)	0.094 (2)	0.0416 (13)	−0.0032 (17)	−0.0048 (13)	−0.0059 (14)
C29	0.114 (2)	0.0783 (18)	0.0509 (14)	0.0014 (15)	0.0051 (14)	−0.0198 (13)
C30	0.0890 (17)	0.0526 (13)	0.0501 (13)	−0.0018 (12)	0.0024 (11)	−0.0066 (10)
N6	0.0822 (18)	0.0880 (19)	0.114 (2)	−0.0055 (17)	−0.0415 (15)	−0.0410 (19)
O1A	0.133 (3)	0.084 (2)	0.150 (4)	−0.005 (2)	−0.085 (3)	0.002 (2)
O2A	0.0728 (18)	0.148 (3)	0.183 (4)	−0.0225 (16)	−0.0267 (17)	−0.064 (2)
O1B	0.15 (2)	0.12 (2)	0.19 (3)	0.075 (19)	−0.081 (19)	−0.08 (2)
O2B	0.27 (3)	0.25 (3)	0.12 (2)	0.09 (2)	−0.13 (2)	−0.109 (19)
N12	0.0526 (11)	0.0481 (11)	0.0804 (13)	−0.0163 (9)	0.0023 (9)	−0.0054 (10)
O3	0.1017 (17)	0.0876 (15)	0.241 (3)	−0.0563 (14)	−0.0743 (18)	0.0496 (17)
O4	0.0612 (10)	0.0490 (10)	0.1066 (14)	−0.0061 (8)	−0.0150 (9)	0.0015 (9)
O17	0.0734 (10)	0.0636 (10)	0.0683 (10)	−0.0249 (8)	0.0213 (8)	−0.0288 (8)
O24	0.0923 (11)	0.0372 (8)	0.0528 (9)	0.0021 (7)	−0.0004 (8)	−0.0066 (7)

Geometric parameters (Å, º)

C1—C5	1.499 (3)	C16—H16A	0.9300
C1—C4	1.569 (3)	C17—O17	1.217 (2)
C1—C2	1.580 (3)	C17—C18	1.491 (3)
C1—H1A	0.9800	C18—C19	1.383 (3)
C2—C11	1.514 (2)	C18—C23	1.384 (3)
C2—C3	1.542 (2)	C19—C20	1.375 (3)
C2—H2A	0.9800	C19—H19A	0.9300
C3—C17	1.519 (3)	C20—C21	1.371 (4)
C3—C4	1.557 (3)	C20—H20A	0.9300
C3—H3A	0.9800	C21—C22	1.368 (4)
C4—C24	1.504 (3)	C21—H21A	0.9300
C4—H4A	0.9800	C22—C23	1.387 (3)
C5—C10	1.390 (3)	C22—H22A	0.9300
C5—C6	1.397 (3)	C23—H23A	0.9300
C6—C7	1.380 (3)	C24—O24	1.217 (2)
C6—N6	1.469 (4)	C24—C25	1.483 (3)
C7—C8	1.359 (5)	C25—C26	1.385 (3)
C7—H7A	0.9300	C25—C30	1.387 (3)
C8—C9	1.372 (4)	C26—C27	1.370 (3)
C8—H8A	0.9300	C26—H26A	0.9300
C9—C10	1.376 (3)	C27—C28	1.369 (4)
C9—H9A	0.9300	C27—H27A	0.9300
C10—H10A	0.9300	C28—C29	1.363 (4)
C11—C16	1.383 (3)	C28—H28A	0.9300
C11—C12	1.401 (3)	C29—C30	1.383 (3)
C12—C13	1.393 (3)	C29—H29A	0.9300
C12—N12	1.460 (3)	C30—H30A	0.9300

C13—C14	1.360 (3)	N6—O1B	1.09 (3)
C13—H13A	0.9300	N6—O1A	1.192 (4)
C14—C15	1.369 (3)	N6—O2A	1.238 (4)
C14—H14A	0.9300	N6—O2B	1.35 (2)
C15—C16	1.384 (3)	N12—O3	1.198 (2)
C15—H15A	0.9300	N12—O4	1.198 (2)

C5—C1—C4	117.35 (16)	C16—C15—H15A	119.7
C5—C1—C2	117.82 (14)	C11—C16—C15	123.0 (2)
C4—C1—C2	88.90 (13)	C11—C16—H16A	118.5
C5—C1—H1A	110.4	C15—C16—H16A	118.5
C4—C1—H1A	110.4	O17—C17—C18	120.32 (18)
C2—C1—H1A	110.4	O17—C17—C3	119.49 (17)
C11—C2—C3	119.52 (15)	C18—C17—C3	119.87 (17)
C11—C2—C1	118.78 (14)	C19—C18—C23	118.94 (19)
C3—C2—C1	90.19 (13)	C19—C18—C17	118.30 (19)
C11—C2—H2A	109.0	C23—C18—C17	122.71 (18)
C3—C2—H2A	109.0	C20—C19—C18	120.4 (2)
C1—C2—H2A	109.0	C20—C19—H19A	119.8
C17—C3—C2	114.65 (15)	C18—C19—H19A	119.8
C17—C3—C4	122.24 (15)	C21—C20—C19	120.4 (2)
C2—C3—C4	90.76 (13)	C21—C20—H20A	119.8
C17—C3—H3A	109.2	C19—C20—H20A	119.8
C2—C3—H3A	109.2	C22—C21—C20	119.9 (2)
C4—C3—H3A	109.2	C22—C21—H21A	120.0
C24—C4—C3	119.06 (15)	C20—C21—H21A	120.0
C24—C4—C1	110.24 (15)	C21—C22—C23	120.2 (2)
C3—C4—C1	90.03 (13)	C21—C22—H22A	119.9
C24—C4—H4A	111.9	C23—C22—H22A	119.9
C3—C4—H4A	111.9	C18—C23—C22	120.1 (2)
C1—C4—H4A	111.9	C18—C23—H23A	119.9
C10—C5—C6	115.99 (19)	C22—C23—H23A	119.9
C10—C5—C1	119.59 (18)	O24—C24—C25	121.40 (17)
C6—C5—C1	124.18 (19)	O24—C24—C4	119.91 (17)
C7—C6—C5	122.2 (3)	C25—C24—C4	118.55 (16)
C7—C6—N6	116.4 (2)	C26—C25—C30	118.15 (19)
C5—C6—N6	121.5 (2)	C26—C25—C24	119.69 (19)
C8—C7—C6	119.8 (3)	C30—C25—C24	122.16 (18)
C8—C7—H7A	120.1	C27—C26—C25	121.0 (2)
C6—C7—H7A	120.1	C27—C26—H26A	119.5
C7—C8—C9	120.1 (2)	C25—C26—H26A	119.5
C7—C8—H8A	120.0	C28—C27—C26	120.0 (2)
C9—C8—H8A	120.0	C28—C27—H27A	120.0
C8—C9—C10	120.0 (3)	C26—C27—H27A	120.0
C8—C9—H9A	120.0	C29—C28—C27	120.2 (2)
C10—C9—H9A	120.0	C29—C28—H28A	119.9
C9—C10—C5	122.0 (2)	C27—C28—H28A	119.9
C9—C10—H10A	119.0	C28—C29—C30	120.1 (2)

C5—C10—H10A	119.0	C28—C29—H29A	120.0
C16—C11—C12	114.61 (17)	C30—C29—H29A	120.0
C16—C11—C2	120.86 (16)	C29—C30—C25	120.5 (2)
C12—C11—C2	124.52 (17)	C29—C30—H30A	119.8
C13—C12—C11	122.70 (19)	C25—C30—H30A	119.8
C13—C12—N12	115.67 (17)	O1A—N6—O2A	124.8 (3)
C11—C12—N12	121.63 (17)	O1B—N6—O2B	114 (2)
C14—C13—C12	120.2 (2)	O1B—N6—C6	129.1 (15)
C14—C13—H13A	119.9	O1A—N6—C6	119.5 (3)
C12—C13—H13A	119.9	O2A—N6—C6	115.7 (3)
C13—C14—C15	119.0 (2)	O2B—N6—C6	111.4 (13)
C13—C14—H14A	120.5	O3—N12—O4	120.1 (2)
C15—C14—H14A	120.5	O3—N12—C12	119.1 (2)
C14—C15—C16	120.5 (2)	O4—N12—C12	120.80 (17)
C14—C15—H15A	119.7		

C5—C1—C2—C11	−6.2 (2)	C14—C15—C16—C11	−1.3 (4)
C4—C1—C2—C11	−126.84 (16)	C2—C3—C17—O17	8.2 (3)
C5—C1—C2—C3	118.12 (17)	C4—C3—C17—O17	116.0 (2)
C4—C1—C2—C3	−2.51 (13)	C2—C3—C17—C18	−178.33 (15)
C11—C2—C3—C17	−107.37 (19)	C4—C3—C17—C18	−70.5 (2)
C1—C2—C3—C17	128.91 (15)	O17—C17—C18—C19	−0.5 (3)
C11—C2—C3—C4	126.25 (17)	C3—C17—C18—C19	−173.92 (18)
C1—C2—C3—C4	2.53 (13)	O17—C17—C18—C23	176.93 (19)
C17—C3—C4—C24	−9.3 (3)	C3—C17—C18—C23	3.5 (3)
C2—C3—C4—C24	110.78 (17)	C23—C18—C19—C20	−0.4 (3)
C17—C3—C4—C1	−122.65 (18)	C17—C18—C19—C20	177.1 (2)
C2—C3—C4—C1	−2.55 (13)	C18—C19—C20—C21	0.3 (4)
C5—C1—C4—C24	120.25 (17)	C19—C20—C21—C22	−0.1 (4)
C2—C1—C4—C24	−118.70 (15)	C20—C21—C22—C23	0.0 (4)
C5—C1—C4—C3	−118.56 (16)	C19—C18—C23—C22	0.4 (3)
C2—C1—C4—C3	2.49 (13)	C17—C18—C23—C22	−177.02 (18)
C4—C1—C5—C10	50.3 (2)	C21—C22—C23—C18	−0.2 (3)
C2—C1—C5—C10	−54.1 (2)	C3—C4—C24—O24	−10.5 (3)
C4—C1—C5—C6	−135.5 (2)	C1—C4—C24—O24	91.3 (2)
C2—C1—C5—C6	120.1 (2)	C3—C4—C24—C25	173.63 (16)
C10—C5—C6—C7	1.4 (4)	C1—C4—C24—C25	−84.5 (2)
C1—C5—C6—C7	−173.0 (2)	O24—C24—C25—C26	−3.1 (3)
C10—C5—C6—N6	−178.7 (2)	C4—C24—C25—C26	172.72 (19)
C1—C5—C6—N6	7.0 (4)	O24—C24—C25—C30	177.2 (2)
C5—C6—C7—C8	−0.5 (5)	C4—C24—C25—C30	−7.0 (3)
N6—C6—C7—C8	179.5 (3)	C30—C25—C26—C27	−0.4 (3)
C6—C7—C8—C9	−0.7 (5)	C24—C25—C26—C27	179.9 (2)
C7—C8—C9—C10	1.0 (5)	C25—C26—C27—C28	0.3 (4)
C8—C9—C10—C5	−0.1 (4)	C26—C27—C28—C29	0.0 (4)
C6—C5—C10—C9	−1.1 (3)	C27—C28—C29—C30	−0.3 (5)
C1—C5—C10—C9	173.6 (2)	C28—C29—C30—C25	0.1 (4)
C3—C2—C11—C16	5.1 (3)	C26—C25—C30—C29	0.2 (3)

C1—C2—C11—C16	113.4 (2)	C24—C25—C30—C29	179.9 (2)
C3—C2—C11—C12	−173.80 (17)	C7—C6—N6—O1B	153 (4)
C1—C2—C11—C12	−65.4 (2)	C5—C6—N6—O1B	−27 (4)
C16—C11—C12—C13	−1.4 (3)	C7—C6—N6—O1A	−137.9 (4)
C2—C11—C12—C13	177.54 (18)	C5—C6—N6—O1A	42.2 (5)
C16—C11—C12—N12	178.28 (18)	C7—C6—N6—O2A	41.9 (4)
C2—C11—C12—N12	−2.8 (3)	C5—C6—N6—O2A	−138.0 (3)
C11—C12—C13—C14	0.5 (3)	C7—C6—N6—O2B	−56 (2)
N12—C12—C13—C14	−179.2 (2)	C5—C6—N6—O2B	124 (2)
C12—C13—C14—C15	0.1 (3)	C13—C12—N12—O3	−9.5 (3)
C13—C14—C15—C16	0.2 (4)	C11—C12—N12—O3	170.8 (3)
C12—C11—C16—C15	1.8 (3)	C13—C12—N12—O4	169.5 (2)
C2—C11—C16—C15	−177.2 (2)	C11—C12—N12—O4	−10.2 (3)