Crystal Structure of Dimethyl-2,6-diaryl-4-*N*-methylcyclohexanimine-1,1-dicarboxylate

S. M. MALATHY SONY,* M. KUPPAYEE,* M. N. PONNUSWAMY,*† V. PADMAVATHI,** and D. BHASKAR REDDY**

*Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai-600 025, India

**Department of Chemistry, Sri Venkateswara University, Tirupati-517502, India

The title compound crystallized in the monoclinic space group *C2/c* with cell parameters $a = 30.812(4)$, $b = 10.840(2)$, $c = 12.401(2)$ Å, $\beta = 106.83(1)^\circ$, $V = 3964.6(11)$ Å³, $Z = 8$, $D_{\text{cal}} = 1.278$ Mg/m³ at $T = 293$ K. The structure was solved by direct methods, and refined by full-matrix least-squares procedures to final $R = 0.0595$ and $wR = 0.1867$ for 2799 reflections. The steric repulsion between the cyclohexane ring and the phenyl substituents at C2 and C6 makes the bond lengths and bond angles slightly abnormal. The cyclohexane ring adopts a twist-boat conformation and the phenyl rings occupy an equatorial orientation. The carboxylate groups are planar with the end methyl atom deviating from planarity. An inter O-H...N, some C-H...O type of intra and intermolecular and an intra C-H... π interactions play a role in stabilizing the molecules in the unit cell.

(Received March 15, 2004; Accepted June 4, 2004; Published on web August 9, 2004)

Biphenyldimethyl-dicarboxylate or colchicine is used in antifibrotic treatments.¹ The cyclohexane triones are a novel group of synthetic antibacterial agents, which are active against gram-positive bacteria, *Haemophilus influenzae* and *Mycobacterium smegmatis*.² The title compound is widely used to synthesize spiro-pyrimidine trione derivatives, because they have a diverse nature of medicinal properties. They have chemotherapeutic properties, such as hypnotic, antitumor, antiviral, anticonvulsant, analgesic and toxic. They also possess bacteriostatic, antidiabetic, antiarrhythmic, antifungal and anti-inflammatory properties.³

The compound dimethyl-2,6-diaryl-4-*N*-methylcyclohexanimine-1,1-dicarboxylate was prepared by the double Michael addition of dimethylmalonate (0.01 mol) to a solution of 1,5-diaryl-1,4-pentadiene-3-imine in 20 ml of methanol. A catalyst of 5% sodium methoxide was added and refluxed for 2 h. Upon cooling and overnight refrigeration, colorless crystals were collected and recrystallized from methanol (Fig. 1).

The structure was solved by direct methods, and refined on F^2 by full-matrix least-squares procedures. The non-hydrogen atoms were refined anisotropically, and all of the hydrogens

were fixed as a riding model over their heavier atoms. The final cycle of refinement converged to $R_1 = 0.0595$ and $wR_1 = 0.1867$ for the observed reflections. The crystal data and the other relevant parameters are given in Table 1. The atomic coordinates along with their equivalent isotropic displacement factors for non-hydrogen atoms are presented in Table 2.

Although the bond lengths C1–C2 and C1–C6 and bond angles around C1, C2 and C6 show only little elongation (Table 3), a similar kind of situation persists in the related structures reported in the literature.⁴ This may be due to a steric repulsion

Fig. 1 Synthetic route for the compound.

Table 1 Crystal and experimental data

Empirical formula	C ₂₂ H ₂₃ NO ₅
Formula weight	381.41
Wavelength	1.54178 Å
Crystal system	monoclinic
Space group, Z	<i>C2/c</i> , 8
Unit cell dimensions	
<i>a</i>	30.812(4) Å
<i>b</i>	10.840(2) Å
<i>c</i>	12.401(2) Å
β	106.83(1)°
Volume	3964.6(11) Å ³
D_x	1.278 Mg/cm ³
Absorption coefficient	0.744 mm ⁻¹
No. of reflections used	3163
$2\theta_{\text{max}}$	62.48° with Cu K_α
<i>R</i> indices [$I > 2\sigma(I)$]	0.0595
$(\Delta\sigma)_{\text{max}}$	0.003
$(\Delta\rho)_{\text{max}}$	0.825
$(\Delta\rho)_{\text{min}}$	-0.378
Measurement	Enraf-Nonius CAD4
Program system	SHELX
Structure determination	direct methods
Refinement	full-matrix least-squares on F^2

†To whom correspondence should be addressed
E-mail: mnpsy@hotmail.com

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) involving non-hydrogen atoms

Atom	x	y	z	U(eq)
C1	1232(1)	2285(2)	7773(2)	38(1)
C2	748(1)	2831(2)	7696(2)	39(1)
C3	595(1)	2462(2)	8722(2)	45(1)
C4	547(1)	1091(2)	8779(2)	43(1)
C5	818(1)	341(2)	8196(2)	47(1)
C6	1282(1)	966(2)	8356(2)	41(1)
C7	1620(1)	118(2)	8032(2)	46(1)
C8	1480(1)	-764(3)	7192(3)	57(1)
C9	1792(1)	-1544(3)	6919(3)	71(1)
C10	2246(1)	-1441(4)	7487(3)	80(1)
C11	2390(1)	-575(4)	8312(3)	80(1)
C12	2079(1)	210(3)	8590(3)	62(1)
C13	695(1)	4215(2)	7497(2)	42(1)
C14	773(1)	5059(3)	8376(2)	53(1)
C15	697(1)	6308(3)	8180(3)	66(1)
C16	539(1)	6738(3)	7098(3)	68(1)
C17	460(1)	5913(3)	6211(3)	67(1)
C18	536(1)	4668(3)	6408(2)	54(1)
C19	1587(1)	3180(2)	8474(2)	45(1)
O20	1753(1)	3096(2)	9475(2)	72(1)
O21	1660(1)	4120(2)	7867(2)	52(1)
C22	1920(1)	5140(3)	8487(3)	77(1)
C23	1273(1)	2107(2)	6577(2)	40(1)
O24	961(1)	1870(2)	5771(2)	61(1)
O25	1703(1)	2151(2)	6556(1)	48(1)
C26	1785(1)	1773(3)	5514(3)	67(1)
N27	294(1)	567(2)	9296(2)	47(1)
O28	77(1)	1441(2)	9819(2)	68(1)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 3 Selected bond lengths ($\text{\AA}$) and bond angles ($^\circ$)

Atoms	Distance	Atoms	Angle
C1 - C6	1.590(3)	C23 - C1 - C19	112.4(2)
C1 - C2	1.581(3)	C23 - C1 - C6	107.6(2)
C19 - O20	1.201(3)	C19 - C1 - C6	110.7(2)
C19 - O21	1.324(3)	C23 - C1 - C2	109.2(2)
O21 - C22	1.449(3)	C19 - C1 - C2	107.6(2)
C23 - O24	1.198(3)	C6 - C1 - C2	109.2(2)
C23 - O25	1.333(3)	C3 - C2 - C13	110.3(2)
O25 - C26	1.445(3)	C3 - C2 - C1	111.3(2)
N27 - O28	1.420(3)	C13 - C2 - C1	115.7(2)
		C7 - C6 - C5	112.3(2)
		C7 - C6 - C1	113.9(2)
		C5 - C6 - C1	111.9(2)

between the cyclohexane ring and the phenyl substituents at the C2 and C6 positions. The packing effects of the carboxylate groups substituted at C1 may also be responsible in defining the bond lengths C1-C2 and C1-C6.

The cyclohexane ring adopts a *twist-boat* conformation where the best plane omits C2 and C5 with the deviation being 0.554(3) and 0.643(3) $\text{\AA}$, respectively. This is also confirmed by puckering amplitude calculations, where $Q_T = 0.7721$. The two phenyl rings, A and B, in the structures are planar and are oriented at an angle of $65.5(1)^\circ$ with respect to each other. The phenyl rings occupy the equatorial orientation and the corresponding torsion angles are [C13-C2-C3-C4 =] $167.3(2)^\circ$ and [C4-C5-C6-C7 =] $166.5(2)^\circ$. The phenyl rings A and B subtend angles of $69.1(1)$ and $70.8(1)^\circ$ with respect to the best plane of the cyclohexane ring. The carboxylate groups at C1 are planar, with the end methyl atom deviating from planarity

Fig. 2 Perspective view of the molecule showing thermal ellipsoids at 30% probability level.

Table 4 Possible non-bonded interactions (hydrogen bonds)

Donor-H...Acceptor	$d(\text{D-H})\text{\AA}$	$d(\text{H}\cdots\text{A})\text{\AA}$	$d(\text{D}\cdots\text{A})\text{\AA}$	$\angle(\text{DHA})^\circ$
C12 - H12 ...O20 ⁱ	0.930(3)	2.898(2)	3.554(4)	128.7(2)
C18 - H18 ...O24 ⁱ	0.930(3)	2.865(2)	3.484(4)	125.1(2)
C2 - H2 ...O20 ⁱⁱ	0.980(2)	2.745(2)	3.724(3)	177.3(1)
C9 - H9 ...O20 ⁱⁱⁱ	0.930(3)	2.610(2)	3.439(4)	148.7(2)
C10 - H10 ...O25 ^{iv}	0.930(4)	2.742(2)	3.462(4)	134.9(3)
C15 - H15 ...O24 ^v	0.930(3)	2.736(2)	3.657(4)	170.6(2)
C16 - H16 ...O28 ^{vi}	0.930(3)	2.799(2)	3.402(4)	123.5(2)
C17 - H17 ...O28 ^{vi}	0.930(3)	2.742(2)	3.379(4)	126.4(2)
O28 - H28 ...N27 ^{vii}	0.820(3)	2.085(2)	2.824(3)	149.9(2)
C26 - H26C ...Cg ⁱ	0.960	3.338	3.766	109.3

Cg (Centroid of phenyl ring A)

Symmetry equivalent positions: (i) x, y, z (ii) $-x, +y, -z + 1/2 + 1$ (iii) $x, -y, +z - 1/2$ (iv) $-x + 1/2, +y - 1/2, -z + 1/2 + 1$ (v) $x, -y + 1, +z + 1/2$ (vi) $x, -y + 1, +z - 1/2$ (vii) $-x, -y, -z + 2$

by $-0.140(4)$ and $-0.132(4)\text{\AA}$; they also differ apart at angles of $61.4(1)^\circ$.

An O-H...N type of intermolecular interaction between the O28 and N27 atoms of $(-x, -y, -z + 2)$ form a dimer along the a -axis. There is a weak intra C-H... π interaction observed between the terminal methyl group and its corresponding side phenyl ring between the atom C26 and the phenyl ring A. C-H...O type of interactions help in the packing of the molecules in a unit cell in addition to van der Waals forces (Table 4).

References

1. P. Liu, Y. Hu, C. Liu, C. Liu, and D. Zhu, *Liver*, **2001**, 21, 384.
2. W. J. Lloyd, A. V. Broadhurst, M. J. Hall, K. J. Andrews, W. E. Barber, and P. Wong-Kal-In, *Antimicrob. Agents Chemother.*, **1988**, 32, 814.
3. D. Bhasker Reddy, V. Padmavathi, and P. V. Ramana Reddy, *Ind. J. Chem.*, **1992**, 31b, 774.
4. P. L. Toupet, and J.C. Messenger, *Acta Cryst.*, **1983**, C39, 750.