The use of the EPSRC X-ray crystallographic service at the University of Wales, Cardiff, Wales, is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BM1041). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 722–724

1,3-Dicyclopropyl-2-(1,2,3-triphenylcyclopropen-3-yl)propane-1,3-dione: a Substituted Cyclopropene with a β-Dicarbonyl Fragment

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(*Received 4 July 1995; accepted 18 September 1995*)

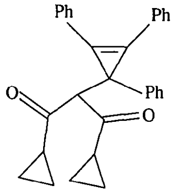
Abstract

The title compound, $C_{30}H_{26}O_2$, has a conformation in which one of the cyclopropanecarbonyl moieties bisects the plane of the cyclopropene ring. The bulky 1,2,3-triphenylcyclopropenyl substituent in the α-position of the β-diketone excludes the possibility of any enolization process. The asymmetry of the single-bond lengths in substituted cyclopropenes, reported previously [Allen (1982). *Tetrahedron*, **38**, 645–655], is not observed in the present compound.

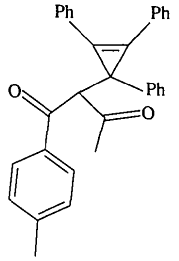
Comment

It is known that cyclopropenyl substituents possess pronounced electron-donating properties (Komendantov, Kostikov, Panasyuk & Domnin, 1987). At the same time, the 1,2,3-triphenylcyclopropenyl group is sterically bulky. Both these factors prevent an enolization process upon introduction of this group in the α-position of dicyclopropanoylmethane.

It has been reported that the presence of an acetyl group in a β-diketone fragment, connected to a 1,2,3-triphenylcyclopropenyl substituent, enables a thermocatalytic isomerization in corresponding substituted cyclopentadienols (Plotkin, Domnin, Dmitrieva & Komendantov, 1987). To the contrary, the title compound does not display such behaviour. Therefore, an X-ray structure determination of the title compound, (I), was undertaken and the results are compared with a crystal structure determination of 1-(4-methylphenyl)-2-(1,2,3-triphenylcyclopropen-3-yl)-butane-1,3-dione, (II) (Fundamenskiy, Starova, Plotkin, Domnin & Yufit, 1989).



(I)



(II)

In actual fact the structures (II) and the title compound, (I), are essentially the same. In both, the acetyl and one of the cyclopropanecarbonyl groups are in a bisected conformation towards the plane of the cyclopropene ring. In each, the phenyl ring at position 1 of the cyclopropene is also in a bisected conformation [the angle between the plane through the cyclopropene ring and that of the phenyl ring C11–C16 is 84.7 (2)° in (II) and 87.5 (5)° in (I)]. In (I), the bond lengths C4—C5 and C4—C6 [1.526 (2) and 1.528 (2) Å] are characteristic of the diketo form, whereas for the enol form the expected values are in the range 1.363–1.400 Å (Emsley, 1984). The bond lengths C5—O5 and C6—O6 are also typical of the diketo form [1.206 (2) and 1.210 (2) Å, respectively]. Moreover, the value of the dihedral angle O5—C5···C6—O6 of the two carbonyl groups is as high as

−55.8 (2)°. Obviously, a comparison of the conformations can not explain the differences in the chemical behaviour of these compounds.

In both of these molecules, as well as in the parent compound 1,2,3-triphenyl-3-isopropylcyclopropene (Domnin, Kopf, Keyaniyan & de Meijere, 1985), no bond-length asymmetry in the cyclopropene single bonds is detected as had been reported by Allen (1982). The values for the title compound are C1—C2 1.516 (2) and C1—C3 1.515 (2) Å. The phenyl rings at the cyclopropene double bond are tilted from the plane of the ring by 6.2 (1) (ring at position 2) and 11.6 (1)° (ring at position 3).

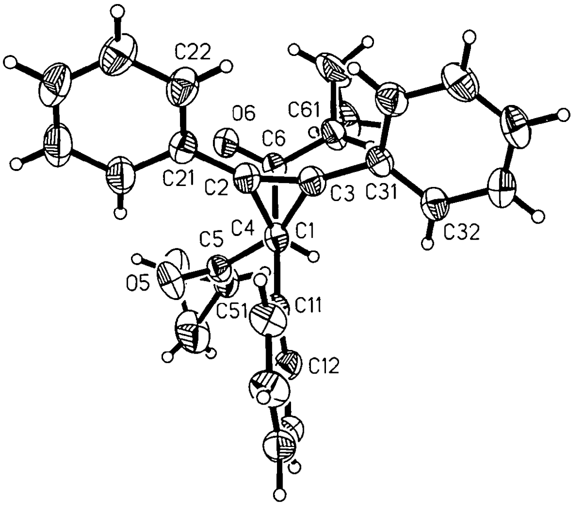


Fig. 1. *ORTEP*II (Johnson, 1976) drawing, as implemented in *SHELXTL-Plus* (Sheldrick, 1992), of the title compound with displacement ellipsoids at 30% probability and atomic numbering scheme. This drawing represents a Newman projection along the C1—C4 single bond with C4 behind C1.

Experimental

The title compound was synthesized according to known procedures (Plotkin, Domnin, Dmitrieva & Komendantov, 1987). Suitable single crystals, melting at 397.5–398 K, were obtained after repeated recrystallizations from ether–pentane mixtures.

Crystal data

$C_{30}H_{26}O_2$
$M_r = 418.51$
Monoclinic
$P2_1/n$
$a = 9.001\ (1)$ Å
$b = 10.321\ (1)$ Å
$c = 25.121\ (2)$ Å
$\beta = 94.85\ (1)°$
$V = 2325.4\ (4)$ Å^3
$Z = 4$
$D_x = 1.195$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 42.9$–$48.8°$
$\mu = 0.571$ mm^{-1}
$T = 293\ (1)$ K
Transparent block
0.6 × 0.4 × 0.4 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6149 measured reflections
4608 independent reflections
4308 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0233$
$\theta_{\rm max} = 76.5°$
$h = -11 \rightarrow 11$
$k = -10 \rightarrow 13$
$l = -31 \rightarrow 31$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0482$
$wR(F^2) = 0.1420$
$S = 1.049$
4608 reflections
339 parameters
H atoms refined with distance restraints (*SHELXL*93; Sheldrick, 1993)
$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2 + 0.4562P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.716$ (for y of C62A)

$\Delta\rho_{\rm max} = 0.233$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.175$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0161 (8)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O5	0.47945 (12)	0.03376 (13)	0.23667 (4)	0.0739 (4)
O6	0.82279 (13)	−0.04374 (11)	0.22556 (5)	0.0739 (3)
C1	0.60003 (14)	0.12936 (13)	0.14325 (5)	0.0480 (3)
C2	0.6183 (2)	0.00607 (14)	0.11164 (5)	0.0526 (3)
C3	0.68717 (15)	0.10675 (14)	0.09508 (5)	0.0511 (3)
C4	0.68156 (14)	0.14363 (13)	0.19918 (5)	0.0471 (3)
C5	0.58814 (14)	0.10175 (14)	0.24414 (5)	0.0509 (3)
C6	0.82396 (15)	0.06241 (14)	0.20516 (5)	0.0518 (3)
C11	0.45711 (15)	0.20526 (14)	0.13357 (5)	0.0501 (3)
C12	0.4135 (2)	0.29993 (15)	0.16834 (6)	0.0593 (4)
C13	0.2815 (2)	0.3681 (2)	0.15762 (7)	0.0685 (4)
C14	0.1917 (2)	0.3449 (2)	0.11168 (7)	0.0720 (4)
C15	0.2347 (2)	0.2533 (2)	0.07647 (7)	0.0793 (5)
C16	0.3644 (2)	0.1842 (2)	0.08739 (6)	0.0693 (4)
C21	0.5679 (2)	−0.12631 (14)	0.10361 (6)	0.0564 (4)
C22	0.6114 (2)	−0.1981 (2)	0.06102 (7)	0.0749 (5)
C23	0.5617 (3)	−0.3234 (2)	0.05224 (9)	0.0882 (6)
C24	0.4702 (3)	−0.3789 (2)	0.08566 (10)	0.0915 (6)
C25	0.4249 (3)	−0.3094 (2)	0.12759 (11)	0.1004 (7)
C26	0.4732 (2)	−0.1832 (2)	0.13724 (8)	0.0790 (5)
C31	0.76244 (15)	0.17614 (14)	0.05500 (5)	0.0509 (3)
C32	0.7722 (2)	0.3097 (2)	0.05692 (6)	0.0602 (4)
C33	0.8383 (2)	0.3778 (2)	0.01779 (7)	0.0739 (5)
C34	0.8945 (2)	0.3132 (2)	−0.02371 (7)	0.0812 (5)
C35	0.8859 (2)	0.1818 (2)	−0.02620 (7)	0.0838 (6)
C36	0.8206 (2)	0.1119 (2)	0.01266 (6)	0.0698 (4)
C51	0.6432 (2)	0.1469 (2)	0.29784 (6)	0.0653 (4)
C52	0.5332 (4)	0.1632 (3)	0.33784 (10)	0.1247 (11)
C53	0.6299 (4)	0.0558 (3)	0.34257 (8)	0.1175 (10)
C61	0.96060 (15)	0.1187 (2)	0.18707 (6)	0.0665 (4)
C62*A*†	1.0989 (9)	0.0408 (13)	0.1917 (5)	0.122 (3)
C63*A*†	1.0798 (6)	0.1356 (8)	0.2310 (2)	0.105 (2)
C62*B*†	1.0513 (9)	0.0267 (7)	0.1581 (3)	0.125 (3)
C63*B*†	1.1071 (7)	0.0691 (11)	0.2092 (4)	0.119 (3)

† Occupancy = 0.5.

Table 2. *Selected geometric parameters (Å, °)*

O5—C5	1.206 (2)	C2—C21	1.448 (2)
O6—C6	1.210 (2)	C3—C31	1.449 (2)
C1—C11	1.508 (2)	C4—C5	1.526 (2)
C1—C3	1.515 (2)	C4—C6	1.528 (2)
C1—C2	1.516 (2)	C5—C51	1.473 (2)
C1—C4	1.536 (2)	C6—C61	1.467 (2)
C2—C3	1.297 (2)		
C3—C1—C2	50.66 (8)	C2—C3—C1	64.72 (10)
C3—C1—C4	120.39 (11)	C5—C4—C6	106.37 (10)
C2—C1—C4	119.67 (11)	C5—C4—C1	113.53 (10)
C3—C2—C1	64.62 (10)	C6—C4—C1	111.66 (11)

Friedel opposites were collected (6559 reflections) and merged to give 4608 symmetry-independent reflections. From the systematic absences ($h0l$, $h + l = 2n$; $0k0$, $k = 2n$) the only possible space group is $P2_1/n$ (No. 14). All H atoms were refined with distance restraints for the C—H distances. Disorder was detected in one cyclopropane ring. Therefore, atoms C62 and C63 were each split over two positions with occupancies of 0.5 for each site. In Fig. 1, only positions C62*A* and C63*A* are drawn.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CADSHEL* (Kopf, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) in *SHELXTL-Plus* (Sheldrick, 1992).

We gratefully acknowledge financial support from the Fonds der Chemischen Industrie. We would also like to thank Dr G. L. Starova for experimental help.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1296). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 724–729

Hexaazatriphenylenehexacarboxamide Solvate Exhibiting π-Complexation in the Solid State

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(*Received 27 October 1994; accepted 9 August 1995*)

Abstract

1,4,5,8,9,12-Hexaazatriphenylene-2,3,6,7,10,11-hexacarboxamide [HAT-(amide)$_6$], $C_{18}H_{12}N_{12}O_6$, has been crystallized from Me$_2$SO/water solutions. The unit cell contains two HAT-(amide)$_6$ molecules, four dimethyl sulfoxide (Me$_2$SO) molecules and one water molecule (formula unit: $C_{18}H_{12}N_{12}O_6.2C_2H_6OS.0.5H_2O$). Pairs of overlapping HAT-(amide)$_6$ molecules form dimers having a one-half ring offset which permits HOMO–LUMO overlap. The C and N atoms of the core rings of one member of the dimer are separated from the best least-squares plane of the core rings of the other member of the dimer by an average distance of 3.31 (9) Å, which is smaller than the sum of the relevant van der Waals radii and is consistent with the π-complexation described by Beeson, Fitzgerald, Gallucci, Gerkin, Rademacher & Czarnik [*J. Am. Chem. Soc.* (1994), **116**, 4621–4622]. Adjacent dimers are separated by a mean distance of 3.69 (9) Å. Some of the amide hydrogen bonds act in concert with the π-complexation in the formation of the dimers. The bond lengths and angles of the HAT core are not uniform. The C—C bonds fall into two distinct groups with means of 1.457 (6) and 1.405 (10) Å; the C—N bonds also fall into two distinct groups with means of 1.350 (2) and 1.322 (7) Å. The 18 atoms comprising the HAT core have a mean deviation of 0.08 (5) Å from the best least-squares plane describing the core. Dihedral angles between the amide-group planes and the least-squares plane of the HAT core range from 10 to 78°. The complex pattern of hydrogen bonding includes intermolecular N—H···O and N—H···N bonds as well as intramolecular N—H···N interactions. Only one cyclic dimer hydrogen-bond is formed. Me$_2$SO and water molecules are involved in the hydrogen-bonding scheme and act also to complete the packing around the HAT-(amide)$_6$ molecules. The mean values of the 16 intermolecular N—H···O hydrogen bond parameters are: N···O 2.99 (19), H···O 2.02 (24) Å, N—H···O 159 (15)°.

Acta Crystallographica Section C
ISSN 0108-2701 ©1996