rise to a few significant differences between corresponding bond distances and bond angles involving these groups.

In the structure of (2), containing the *cis*-1,2-disubstituted cyclohexane moiety, the hydrogen bonds between the molecules form closed loops (Fig. 4) in which only one amide group of each conformer is involved. The crystal structure consists of hydrogen-bonded hexamers, held together by weak van der Waals forces.

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Structure of 7,8-Bis(3,3-dimethyl-1-butynyl)-*cis-anti-cis*-tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione

By Hans-Jürgen Rathjen, William C. Agosta* and Paul Margaretha†

Institut für Organische Chemie der Universität, M. L. King Platz 6, *D*-2000 *Hamburg* 13, *Germany*

and Anne-Marie Chiu, Louis Todaro and Steven Wolff

Chemical Research Department, Hoffmann–La Roche Inc., 340 *Kingsland Street, Nutley, New Jersey* 07110, *USA*

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Abstract. $C_{24}H_{32}O_2$, $M_r = 352{\cdot}52$, tetragonal, $P4_32_12$, $a = 11{\cdot}526\ (2)$, $c = 49{\cdot}982\ (7)$ Å, $V = 6640\ (3)$ Å^3, $Z = 12$, $D_x = 1{\cdot}06$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}47$ mm^{-1}, $F(000) = 2304$, $T = 110$ K, $R = 0{\cdot}048$, $wR = 0{\cdot}060$ for 5957 observed reflections. There are one and a half independent molecules of the title compound in the asymmetric unit cell. The cyclobutane ring shows a very similar degree of puckering ($\alpha = 147°$) compared to other tricyclo[6.4.0.0^{2,7}]dodecanes with analogous configuration and alkyl-substitution patterns.

Introduction. Cyclohex-2-enones undergo [2 + 2] photocycloaddition with alkenes affording bicyclo[4.2.0]octan-2-ones, while in the absence of alkenes irradiation in polar solvents leads to (dimeric) tricyclo[6.4.0.0^{2,7}]dodecan-3,12-diones (Anklam, König & Margaretha, 1983, and references cited therein). We have recently shown that 3-(alk-1-ynyl)cyclohex-2-enones afford both [2 + 2] and [3 + 2] photocycloadducts on iradiation in the presence of either 2,3-dimethylbut-2-ene (Margaretha, Rathjen, Wolff & Agosta, 1988) or 1,1-dimethoxy-2-methylpropene (Margaretha, Rathjen & Agosta, 1990), all products resulting from a common 1,4-alkylpropargyl biradical (1), which undergoes either 1,4- or 1,5-

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* Laboratories of The Rockefeller University, New York.

† To whom correspondence should be addressed.

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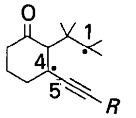
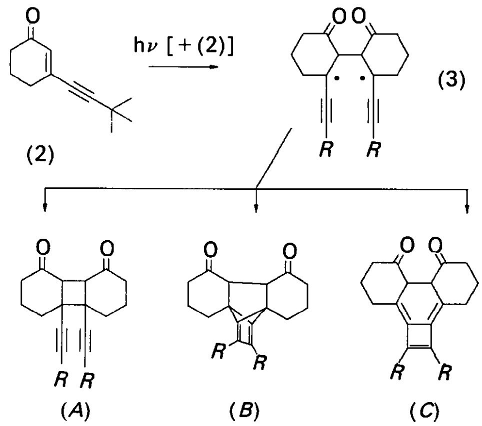
cyclization. In this context it was of interest to investigate the behaviour of excited 3-(alk-1-ynyl)-cyclohex-2-enones, *e.g.* (2), in the absence of alkenes. Indeed, biradical (3) could cyclize to either a [2 + 2] dimer (*A*), to a bis-[3 + 2] dimer (*B*) or to a [3 + 3] dimer (*C*). Irradiation ($\lambda = 350$ nm) of 3-(3,3-dimethylbut-1-ynyl)cyclohex-2-enone (2) in *tert*-butanol affords one dimer (4), m.p. 380–381 K (from pentane) in 68% yield. The ^{1}H NMR and ^{13}C NMR spectra indicate a symmetric structure. The present study has been made in order to determine the structure of the photodimer of (2) and confirms that (4) is an (*A*)-type dimer with HH (head-to-head) constitution and *cis-anti-cis* configuration.



(1)



R = C(CH$_3$)$_3$

Experimental. Crystals of dimer (4) were obtained by slow evaporation from hexane solution, m.p. 381 K, ^{13}C NMR (CDCl$_3$): δ, 209·2(*s*), 94·1(*s*), 79·4(*s*), 51·2(*d*), 44·3(*s*), 38·5(*t*), 32·3(*t*), 31·2(*q*), 27·0(*s*), 21·2(*t*). ^{1}H NMR (CDCl$_3$): δ, 3·00 (*s*, 2H), 2·5–1·8 (*m*, 12H), 1·20 (*s*, 18H). MS: *m*/*z*, 352 (M^+, 3%), 176 (100%). The crystal used for X-ray data collection, approximately 0·30 × 0·40 × 0·60 mm, was cooled in a nitrogen gas stream to 110 K. The intensity data were measured on an Enraf–Nonius CAD-4 diffractometer (graphite-monochromated Cu $K\alpha$ radiation). The cell parameters were determined by least-squares refinement against the setting angles of 25 reflections within $11{\cdot}4 \le 2\theta \le 22{\cdot}3°$. Intensity data were measured by $\omega/2\theta$ scans ($2{\cdot}0 < 2\theta < 150°$; $0 \le h \le 14$, $0 \le k \le 14$, $0 \le l \le 62$). The data were not corrected for absorption. Two standard reflections with < 5% variation in intensity. Of the 6849 independent reflections, 5957 were considered to be observed [$I > 3{\cdot}0\sigma(I)$].

Table 1. *Final atomic and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}(Å^2)
O(3)	0·5933 (1)	0·5253 (2)	0·4209 (1)	0·040 (1)
O(12)	0·7059 (2)	0·8126 (2)	0·4355 (1)	0·045 (1)
C(1)	0·8427 (2)	0·6762 (2)	0·4205 (1)	0·021 (1)
C(2)	0·7963 (2)	0·5499 (2)	0·4252 (1)	0·022 (1)
C(3)	0·6877 (2)	0·5149 (2)	0·4103 (1)	0·028 (1)
C(4)	0·7012 (2)	0·4701 (2)	0·3822 (1)	0·038 (1)
C(5)	0·8142 (2)	0·4041 (2)	0·3778 (1)	0·039 (1)
C(6)	0·9170 (2)	0·4808 (2)	0·3856 (1)	0·024 (1)
C(7)	0·9170 (2)	0·5048 (2)	0·4157 (1)	0·020 (1)
C(8)	0·9687 (2)	0·6280 (2)	0·4231 (1)	0·020 (1)
C(9)	1·0110 (2)	0·6359 (2)	0·4522 (1)	0·024 (1)
C(10)	0·9975 (2)	0·7602 (2)	0·4623 (1)	0·032 (1)
C(11)	0·8697 (2)	0·7908 (2)	0·4648 (1)	0·034 (1)
C(12)	0·7987 (2)	0·7660 (2)	0·4400 (1)	0·029 (1)
C(71)	0·9599 (2)	0·4042 (2)	0·4307 (1)	0·023 (1)
C(72)	0·9893 (2)	0·3206 (2)	0·4430 (1)	0·026 (1)
C(73)	1·0260 (2)	0·2195 (2)	0·4590 (1)	0·033 (1)
C(74)	1·1570 (2)	0·2273 (3)	0·4640 (1)	0·056 (1)
C(75)	0·9970 (3)	0·1079 (2)	0·4435 (1)	0·049 (1)
C(76)	0·9595 (2)	0·2204 (2)	0·4856 (1)	0·041 (1)
C(81)	1·0543 (2)	0·6809 (2)	0·4052 (1)	0·023 (1)
C(82)	1·1242 (2)	0·7347 (2)	0·3927 (1)	0·025 (1)
C(83)	1·2147 (2)	0·8040 (2)	0·3790 (1)	0·026 (1)
C(84)	1·1629 (2)	0·8692 (2)	0·3550 (1)	0·036 (1)
C(85)	1·3118 (2)	0·7239 (2)	0·3697 (1)	0·041 (1)
C(86)	1·2621 (2)	0·8925 (2)	0·3993 (1)	0·042 (1)
O(3′)	0·8015 (1)	0·5442 (2)	0·4975 (1)	0·038 (1)
C(2′)	0·6006 (2)	0·5088 (2)	0·4951 (1)	0·020 (1)
C(3′)	0·7171 (2)	0·5051 (2)	0·5089 (1)	0·024 (1)
C(4′)	0·7231 (2)	0·4497 (2)	0·5359 (1)	0·028 (1)
C(5′)	0·6466 (2)	0·3412 (2)	0·5377 (1)	0·028 (1)
C(6′)	0·5206 (2)	0·3706 (2)	0·5311 (1)	0·024 (1)
C(7′)	0·5085 (2)	0·4126 (2)	0·5018 (1)	0·021 (1)
C(71′)	0·5119 (2)	0·3144 (2)	0·4833 (1)	0·023 (1)
C(72′)	0·5276 (2)	0·2351 (2)	0·4684 (1)	0·024 (1)
C(73′)	0·5611 (2)	0·1368 (2)	0·4515 (1)	0·025 (1)
C(74′)	0·4543 (2)	0·0739 (2)	0·4402 (1)	0·038 (1)
C(75′)	0·6382 (2)	0·1801 (2)	0·4285 (1)	0·041 (1)
C(76′)	0·6310 (2)	0·0521 (2)	0·4691 (1)	0·039 (1)

The structure was solved by a multi-solution (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) procedure and refined by full-matrix least squares on *F*. In the final refinement, $\sum w(|F_o| - |F_c|)^2$ being minimized, the non-H atoms were refined anisotropically. The H atoms were included in the structure-factor calculations but their parameters were not refined. The final discrepancy indices are $R = 0{\cdot}048$ and $wR = 0{\cdot}060$ for the 5957 observed reflections. 352 parameters, $w = [1/\sigma^2(|F_o|)]$, $\Delta/\sigma_{\max} = 0{\cdot}37$. The final difference map has no peaks greater than $\pm 0{\cdot}6$ e Å^{-3}. Scattering factors from *SHELX*76.

Discussion. Final atomic parameters are given in Table 1, bond distances and angles are reported in Table 2.* There are one and a half independent molecules of the title compound in the asymmetric unit cell. Fig. 1 shows a view of one molecule of

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* Tables of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54177 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and bond angles* (°) *for* (4) *with e.s.d.'s in parentheses*

O(3)	C(3)	1·217 (2)	C(73)	C(76)	1·537 (3)
O(12)	C(12)	1·218 (3)	C(81)	C(82)	1·195 (3)
C(1)	C(2)	1·569 (3)	C(82)	C(83)	1·480 (3)
C(1)	C(8)	1·561 (3)	C(83)	C(84)	1·537 (3)
C(1)	C(12)	1·508 (3)	C(83)	C(85)	1·537 (3)
C(2)	C(3)	1·513 (3)	C(83)	C(86)	1·533 (3)
C(2)	C(7)	1·559 (3)	O(3′)	C(3′)	1·213 (2)
C(3)	C(4)	1·505 (3)	C(1′)	C(2′)	1·573 (2)
C(4)	C(5)	1·524 (3)	C(2′)	C(3′)	1·508 (3)
C(5)	C(6)	1·529 (3)	C(2′)	C(7′)	1·570 (2)
C(6)	C(7)	1·533 (2)	C(3′)	C(4′)	1·497 (3)
C(7)	C(8)	1·583 (3)	C(4′)	C(5′)	1·533 (3)
C(7)	C(71)	1·465 (3)	C(5′)	C(6′)	1·528 (3)
C(8)	C(9)	1·537 (3)	C(6′)	C(7′)	1·545 (3)
C(8)	C(81)	1·465 (3)	C(7′)	C(8′)	1·574 (2)
C(9)	C(10)	1·527 (3)	C(7′)	C(71′)	1·465 (3)
C(10)	C(11)	1·520 (3)	C(71′)	C(72′)	1·192 (3)
C(11)	C(12)	1·512 (3)	C(72′)	C(73′)	1·465 (3)
C(71)	C(72)	1·194 (3)	C(73′)	C(74′)	1·536 (3)
C(72)	C(73)	1·473 (3)	C(73′)	C(75′)	1·541 (3)
C(73)	C(74)	1·534 (3)	C(73′)	C(76′)	1·536 (3)
C(73)	C(75)	1·539 (3)			

C(2)	C(1)	C(8)	88·5 (1)	C(74)	C(73)	C(75)	110·2 (2)
C(2	C(1)	C(12)	115·2 (2)	C(74)	C(73)	C(76)	110·3 (2)
C(8)	C(1)	C(12)	120·2 (2)	C(75)	C(73)	C(76)	109·5 (2)
C(1)	C(2)	C(3)	117·1 (2)	C(8)	C(81)	C(82)	172·3 (2)
C(1)	C(2)	C(7)	87·7 (1)	C(81)	C(82)	C(83)	175·7 (2)
C(3)	C(2)	C(7)	120·0 (2)	C(82)	C(83)	C(84)	110·4 (2)
O(3)	C(3)	C(2)	119·9 (2)	C(82)	C(83)	C(85)	109·4 (2)
O(3)	C(3)	C(4)	122·3 (2)	C(82)	C(83)	C(86)	107·8 (2)
C(2)	C(3)	C(4)	117·8 (2)	C(84)	C(83)	C(85)	110·0 (2)
C(3)	C(4)	C(5)	113·2 (2)	C(84)	C(83)	C(86)	110·1 (2)
C(4)	C(5)	C(6)	109·7 (2)	C(85)	C(83)	C(86)	109·1 (2)
C(5)	C(6)	C(7)	110·7 (2)	C(1′)	C(2′)	C(3′)	118·5 (1)
C(2)	C(7)	C(6)	111·1 (1)	C(1′)	C(2′)	C(7′)	87·4 (1)
C(2)	C(7)	C(8)	88·0 (1)	C(3′)	C(2′)	C(7′)	119·0 (1)
C(2)	C(7)	C(71)	114·2 (1)	O(3′)	C(3′)	C(2′)	119·4 (2)
C(6)	C(7)	C(8)	113·0 (1)	O(3′)	C(3′)	C(4′)	123·0 (2)
C(6)	C(7)	C(71)	111·0 (2)	C(2′)	C(3′)	C(4′)	117·6 (2)
C(8)	C(7)	C(71)	117·6 (1)	C(3′)	C(4′)	C(5′)	111·9 (2)
C(1)	C(8)	C(7)	87·2 (1)	C(4′)	C(5′)	C(6′)	110·6 (2)
C(1)	C(8)	C(9)	110·7 (1)	C(5′)	C(6′)	C(7′)	111·1 (2)
C(1)	C(8)	C(81)	115·3 (2)	C(2′)	C(7′)	C(6′)	111·2 (1)
C(7)	C(8)	C(9)	113·2 (1)	C(2′)	C(7′)	C(8′)	87·4 (1)
C(7)	C(8)	C(81)	119·0 (1)	C(2′)	C(7′)	C(71′)	113·1 (2)
C(9)	C(8)	C(81)	109·8 (2)	C(6′)	C(7′)	C(8′)	113·2 (1)
C(8)	C(9)	C(10)	109·7 (2)	C(6′)	C(7′)	C(71′)	110·7 (1)
C(9)	C(10)	C(11)	110·1 (2)	C(8′)	C(7′)	C(71′)	119·2 (2)
C(10)	C(11)	C(12)	114·5 (2)	C(7′)	C(71′)	C(72′)	172·8 (2)
O(12)	C(12)	C(1)	118·6 (2)	C(71′)	C(72′)	C(73′)	173·0 (2)
O(12)	C(12)	C(11)	122·9 (2)	C(72′)	C(73′)	C(74′)	111·5 (2)
C(1)	C(12)	C(11)	118·5 (2)	C(72′)	C(73′)	C(75′)	107·4 (2)
C(7)	C(71)	C(72)	176·7 (2)	C(72′)	C(73′)	C(76′)	109·4 (2)
C(71)	C(72)	C(73)	178·4 (2)	C(74′)	C(73′)	C(75′)	109·3 (2)
C(72)	C(73)	C(74)	109·0 (2)	C(74′)	C(73′)	C(76′)	110·0 (2)
C(72)	C(73)	C(75)	109·1 (2)	C(75′)	C(73′)	C(76′)	109·2 (2)
C(72)	C(73)	C(76)	108·7 (2)				

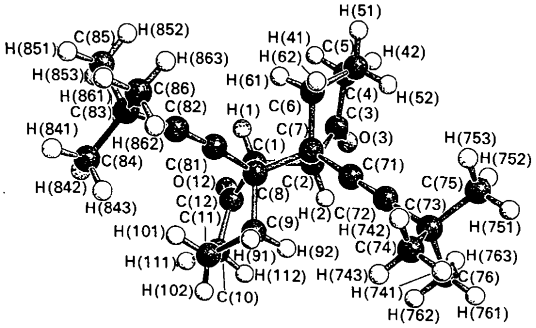

Fig. 1. *SCHAKAL*88 (Keller, 1986) view of one molecule of photodimer (4), showing the atom-numbering scheme.

photodimer (4) and illustrates the atom-numbering scheme chosen [the atom numbers of the second (half) molecule follow the same scheme with primed numbers, *cf.* Tables 1 and 2]. The unprimed molecule is not related by crystallographic symmetry to the (half) primed molecule. Half of the primed molecule, however, is related to the other half by a crystallographic twofold rotation axis. The corresponding distances and angles of the two independent molecular units compare very well with average deviations of 0·005 (4) Å and 0·7 (4)°, respectively.

The dihedral angle of the (central) four-membered ring α, defined as C(7)C(2)C(1) ∩ C(7)C(8)C(1), of (4) (147°) is almost identical with that for the HH-*cis-anti-cis* dimer of 3,5,5-trimethylcyclohex-2-en-1-ol ($\alpha = 146°$) (Koning, Visser & Vos, 1970) and very similar to that for the HH-*cis-anti-cis* dimer of 2,2,6-trimethyl-3,4-dihydro-2*H*-pyran-4-one ($\alpha = 154°$) (Anklam, König, Margaretha & Schmalle, 1984). These values correspond to those measured by either electron diffraction (Almenningen, Bastiansen & Skancke, 1961) or by ^{1}H NMR (Lambert & Roberts, 1965) for non-fused (monocyclic) cyclobutanes. In contrast, in both the *syn-* and *anti*-HT-dimers of 3,5,5-trimethylcyclohex-2-enone the four-membered ring is nearly planar (Johnson & Vos, 1968). More data is nevertheless required in order to correlate unequivocally the degree of puckering of the central cyclobutane ring with the constitution of tricyclo[6.4.0.0^{2,7}]dodecanediones and related compounds.

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