



A Chiral N-Crotonyloxazolidinone Diels-Alder Adduct

Citation

Marsh, Richard E., William P. Schaefer, Paivi J. Kukkola and Andrew G. Myers. 1992. A chiral n-crotonyloxazolidinone diels-alder adduct. Acta Crystallographica Section C: Crystal Structure Communications C48(9): 1622-1624.

Published Version

<http://dx.doi.org/10.1107/S0108270192000738>

Permanent link

<http://nrs.harvard.edu/urn-3:HUL.InstRepos:3122539>

Terms of Use

This article was downloaded from Harvard University's DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at <http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA>

Share Your Story

The Harvard community has made this article openly available.
Please share how this access benefits you. [Submit a story](#).

[Accessibility](#)

The present crystal structure analysis shows that the absolute configuration at C(4) is *R* and at C(17), *S*.

References

- BOUVIER, P., ANDRIEUX, J., CUNHA, H. & MOLHO, D. (1977). *Bull. Chim. Soc. Fr.* pp. 1187–1194.
 CLARKE-LEWIS, J. W., ILSELEY, A. H. & MCGARRY, E. J. (1976). *Aust. J. Chem.* **29**, 2741–2746.

- FUJIMOTO, A. & SAKURAI, A. (1977). *Synthesis*, pp. 871–872.
 HARRISON, D. M. (1979). *Comprehensive Organic Chemistry*, Vol. 4, edited by D. BARTON, & W. D. OLLIS, pp. 765–766. Oxford: Pergamon Press.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 JURD, L. & WAISS, A. C. JR (1968). *Tetrahedron*, **24**, 2801–2808.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Acta Cryst. (1992). **C48**, 1622–1624

A Chiral *N*-Crotonyloxazolidinone Diels–Alder Adduct

BY RICHARD E. MARSH, WILLIAM P. SCHAEFER, PAIVI J. KUKKOLA AND ANDREW G. MYERS

Division of Chemistry and Chemical Engineering and The Beckman Institute, Mail Code 139-74, California Institute of Technology, Pasadena, California 91125, USA*

(Received 7 August 1991; accepted 14 January 1992)

Abstract. (4*S*)-4-Benzyl-3-[(4*S*,5*S*)-(1-methoxy-5-methylcyclohexen-4-yl)carbonyl]-2-oxazolidinone, C₁₉H₂₃NO₄, *M_r* = 329.40, monoclinic, *P*2₁, *a* = 11.453 (3), *b* = 7.163 (4), *c* = 11.929 (2) Å, β = 111.86 (2)°, *V* = 908.3 (5) Å³, *Z* = 2, *D_x* = 1.20 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 0.79 cm⁻¹, *F*(000) = 352, *T* = 297 K, *R* = 0.034 for 885 reflections with *F_o*² > 0. The molecule is extended in the crystal; there is a small twist, -13.1 (2)°, about the amide-like C–N bond joining the oxazolidinone ring to the carbonyl group. The configurations at the two optical centers in the cyclohexene ring confirm the anticipated stereospecificity of the Diels–Alder cycloaddition synthesis.

Introduction. In a study of the Diels–Alder reaction of 2-methoxy-1,3-butadiene with 4-benzyl-3-crotonyl-2-oxazolidinone of known absolute stereochemistry [4*S* (Myers & Kukkola, 1991)], the conditions that we developed for optimum diastereoselectivity and yield deviated substantially from reported literature procedures for analogous substrates (Evans, Chapman & Bisaha, 1988). Accordingly, the relative stereochemistry of the cycloadduct (1) which we synthesized could not be confidently assigned by analogy with earlier examples. As reported herein, the structure of (1) is established by X-ray crystallography as (4*S*)-4-benzyl-3-[(4*S*,5*S*)-(1-methoxy-5-methylcyclohexen-4-yl)carbonyl]-2-oxazolidinone. Cycloaddition under the modified

conditions thus proceeds with the same stereochemical sense as related substrates under the original protocol of Evans *et al.* (1988).

Experimental. A diamond-shaped plate crystal, 0.16 × 0.23 × 0.09 mm, was used for data collection on a CAD-4 diffractometer with ω scans. Cell dimensions were determined from 25 reflections with 28 < 2θ < 35°. No absorption correction was applied (μ_{r,max} = 0.01). (sinθ/λ)_{max} = 0.48 Å⁻¹; *h* from -10 to 10, *k* from -6 to 6, *l* from 0 to 10; two check reflections (212̄ and 302̄) decayed 14% and 15%, respectively, during the 52 h of data collection and a quadratic correction was applied. 3500 reflections were measured, those to θ = 17.5° four times, and those from 17.5 to 20° twice. 925 independent reflections were measured; goodness of fit for merging was 0.985 (*R*_{merge} = 0.038 for 266 reflections with exactly two observations). All reflections were used in solution and refinement of the structure. The structure was solved by Patterson methods plus structure factor–Fourier calculations [*MULTAN*88 (Debaeremaeker, Germain, Main, Refaat, Tate & Woolfson, 1988) did not readily give a solution], *F*² values, positive and negative, were used in the refinement with weights = 1/σ²(*F_o*²). H atoms were positioned by calculation (C–H = 0.95 Å), assuming a staggered conformation for C12; H-atom parameters were not refined but adjusted once, near the end of the refinement. Coordinates (except *y* of N) and anisotropic displacement parameters of all non-H atoms, a scale factor and a secondary-extinction

* Contribution No. 8475.

Table 1. Final heavy-atom coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for $C_{19}H_{23}NO_4$

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

	x	y	z	U_{eq}
N	-3760 (3)	-1334	-734 (3)	523 (10)
C1	-4454 (5)	-1555 (9)	-7 (5)	625 (14)
O1	-5678 (3)	-1602 (6)	-722 (3)	883 (11)
O2	-4084 (3)	-1709 (7)	1069 (3)	773 (9)
C2	-5827 (4)	-1163 (9)	-1945 (5)	887 (17)
C3	-4567 (4)	-1588 (8)	-2012 (3)	558 (13)
C4	-2475 (4)	-949 (8)	-372 (4)	583 (14)
O3	-1996 (3)	-1091 (7)	-1115 (3)	848 (10)
C5	-1779 (4)	-256 (8)	896 (4)	523 (12)
C6	-915 (4)	1375 (8)	924 (4)	587 (12)
C7	-345 (4)	2090 (8)	2222 (4)	687 (15)
C8	79 (4)	564 (10)	3133 (4)	685 (16)
C9	-197 (4)	-1197 (8)	2912 (4)	716 (15)
C10	-1024 (4)	-1860 (8)	1676 (4)	703 (14)
C11	-1574 (4)	2950 (8)	67 (4)	768 (14)
O4	776 (3)	1315 (7)	4243 (3)	932 (12)
C12	1325 (5)	58 (10)	5226 (5)	1160 (21)
C13	-4487 (4)	-3539 (8)	-2490 (4)	585 (13)
C14	-5445 (4)	-3772 (8)	-3763 (4)	517 (13)
C15	-6518 (5)	-4790 (8)	-3972 (4)	673 (15)
C16	-7426 (4)	-4940 (9)	-5133 (6)	792 (16)
C17	-7251 (5)	-4077 (10)	-6080 (5)	817 (18)
C18	-6187 (6)	-3053 (8)	-5874 (5)	777 (18)
C19	-5278 (5)	-2918 (8)	-4719 (5)	696 (16)

Table 2. Distances (\AA) and angles ($^\circ$) not involving H atoms for $C_{19}H_{23}NO_4$

N—C1	1.386 (7)	C6—C11	1.521 (7)
N—C3	1.470 (6)	C7—C8	1.490 (8)
N—C4	1.398 (6)	C8—C9	1.303 (8)
C1—O1	1.343 (7)	C8—O4	1.376 (7)
C1—O2	1.197 (7)	C9—C10	1.502 (7)
O1—C2	1.440 (7)	O4—C12	1.425 (7)
C2—C3	1.506 (7)	C13—C14	1.515 (7)
C3—C13	1.525 (7)	C14—C15	1.370 (7)
C4—O3	1.209 (6)	C14—C19	1.369 (7)
C4—C5	1.507 (7)	C15—C16	1.392 (8)
C5—C6	1.524 (7)	C16—C17	1.367 (9)
C5—C10	1.528 (7)	C17—C18	1.363 (9)
C6—C7	1.528 (7)	C18—C19	1.388 (8)
C3—N—C1	110.4 (4)	C11—C6—C5	113.4 (4)
C4—N—C1	127.7 (4)	C11—C6—C7	110.5 (4)
C4—N—C3	121.8 (4)	C8—C7—C6	113.2 (4)
O1—C1—N	108.2 (5)	C9—C8—C7	125.0 (5)
O2—C1—N	128.7 (5)	O4—C8—C7	109.3 (5)
O2—C1—O1	123.2 (5)	O4—C8—C9	125.7 (5)
C2—O1—C1	109.8 (4)	C10—C9—C8	121.4 (5)
C3—C2—O1	104.8 (4)	C9—C10—C5	111.6 (4)
C2—C3—N	99.5 (4)	C12—O4—C8	117.7 (4)
C13—C3—N	113.6 (4)	C14—C13—C3	110.8 (4)
C13—C3—C2	113.4 (4)	C15—C14—C13	120.5 (4)
O3—C4—N	118.1 (4)	C19—C14—C13	120.8 (4)
C5—C4—N	118.5 (4)	C19—C14—C15	118.7 (5)
C5—C4—O3	123.3 (4)	C16—C15—C14	120.6 (5)
C6—C5—C4	111.8 (4)	C17—C16—C15	120.2 (5)
C10—C5—C4	109.4 (4)	C18—C17—C16	119.4 (6)
C10—C5—C6	110.3 (4)	C19—C18—C17	120.4 (5)
C7—C6—C5	108.0 (4)	C18—C19—C14	120.7 (5)

parameter, were refined in one full matrix. $R = 0.034$ for 885 reflections with $F_o^2 > 0$, 0.026 for 753 reflections with $F_o^2 > 3\sigma(F_o^2)$, wR (on F^2) = 0.003, $S = 1.50$ for 925 reflections and 217 parameters. Variances $[\sigma^2(I)]$ were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data by propagation of error plus another additional term, $(0.014I)^2$. In the final least-squares cycle the largest shift was less than 0.01 times its standard deviation. In the final difference map the

largest peak was $0.12 e \text{\AA}^{-3}$ and the largest hole, $-0.12 e \text{\AA}^{-3}$. The secondary-extinction correction (Larson, 1967) refined to $2.2(3) \times 10^{-6}$. Atomic scattering factors were taken from Cromer & Waber (1974); computer programs used were those of the *CRYM* crystallographic computing system (Duchamp, 1964). Final refined parameters of the atoms are given in Table 1.*

The compound was synthesized from an optically-pure oxazolidinone whose configuration was known. Our original model had the opposite hand, so for the final refinement it was inverted to the structure described here. The object of the diffraction study, then, was simply to determine the relative configurations of the optically pure product; the absolute configuration was obtained by comparison with the known absolute configuration of the starting material.

* Lists of anisotropic displacement parameters, complete distances and angles, observed and calculated structure factors and assigned H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55054 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0568]

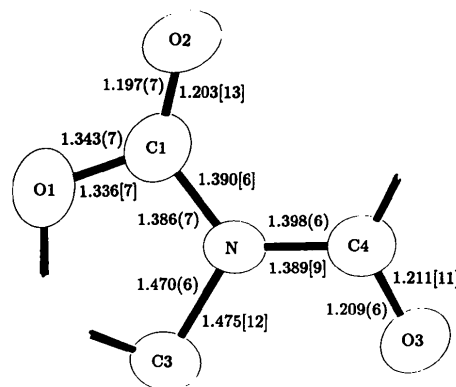


Fig. 1. The central portion of the molecule with bond distances (\AA) shown, compared to the averages found for the comparable molecules referenced in the text; these latter distances are shown with scatter standard deviations in brackets.

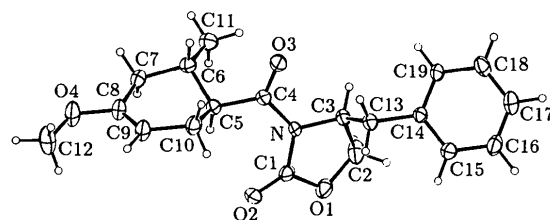


Fig. 2. An ORTEP (Johnson, 1976) drawing of the molecule showing the numbering system with 20% probability ellipsoids. H atoms are shown as open circles of arbitrary (small) size.

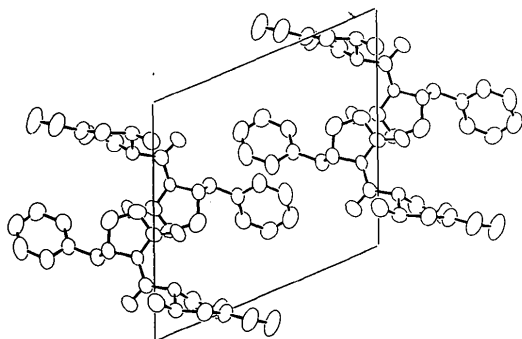


Fig. 3. An ORTEP (Johnson, 1976) drawing of four molecules (the contents of two unit cells) with one unit cell outlined, viewed down the *b* axis. H atoms are not shown.

Discussion. This oxazolidinone has structural features that are comparable to those of similar compounds. Individual bond distances and angles (Table 2) fall within normal ranges and, for the oxazolidinone system, the geometry is like that seen by others (Walba, Thurmes & Haltiwanger, 1988; Abdel-Magid, Pridgen, Eggleston & Lantos, 1986; Nakai, 1988; Baker, Cooke, Humphrey, Wright & Hirshfield, 1987; Molander & Kenny, 1989; Herold, Duthaler, Riks & Angst, 1989). For these compounds, distances in the oxazolidinone system are shown in Fig. 1 (with sample standard deviations in brackets), along with the distances observed for this structure. The atoms involved in these distances are nearly planar: ± 0.11 Å for the structure reported by Nakai (1988) (better for all other reference compounds), ± 0.14 Å for the present structure. There is a twist of about -13° about the N—C4 bond that is primarily responsible for the departures from planarity, but even the fragment O1, C1, N, C3, C4 has atoms up to ± 0.09 Å from their plane, so the situation is not a simple one. Fig. 2 shows the complete molecule.

There are six contacts between symmetry-related molecules of less than 3.6 Å, all from methyl, methylene or benzene C atoms to O atoms, although only one of these [C16...O4 at $x-1, y-1, z-1$, 3.294 (7) Å] is short enough to imply a weak C—H...O hydrogen bond. The other contacts represent weaker interactions. Some of these interactions can be seen in Fig. 3.

AGM and PJK gratefully acknowledge the generous support of the National Institutes of Health, ICI Americas Inc., and Monsanto Company.

References

- ABDEL-MAGID, A., PRIDGEN, L. N., EGGLESTON, D. S. & LANTOS, I. (1986). *J. Am. Chem. Soc.* **108**, 4595–4602.
- BAKER, R., COOKE, H. G. HUMPHREY, G. R., WRIGHT, S. H. B. & HIRSHFIELD, J. (1987). *J. Chem. Soc. Chem. Commun.* pp. 1102–1104.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101. Birmingham; Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- DEBAERDEMAEKER, T., GERMAIN, G., MAIN, P., REFAAT, L. S., TATE, C. & WOOLFSON, M. M. (1988). *MULTAN88. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England.
- DUCHAMP, D. J. (1964). *CRYM* crystallographic computing system. Am. Crystallogr. Assoc. Meet., Bozeman, Montana. Paper B14, p. 29.
- EVANS, D. A., CHAPMAN, K. T. & BISAHA, J. (1988). *J. Am. Chem. Soc.* **110**, 1238–1256.
- HEROLD, P., DUTHALER, R., RIKS, G. & ANGST, C. (1989). *J. Org. Chem.* **54**, 1178–1185.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-3794, third version. Oak Ridge National Laboratory, Tennessee, USA.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- MOLANDER, G. A. & KENNY, C. (1989). *J. Am. Chem. Soc.* **111**, 8236–8246.
- MYERS, A. G. & KUKKOLA, P. J. (1991). Unpublished results.
- NAKAI, H. (1988). *Acta Cryst.* **C44**, 2215–2217.
- WALBA, D. M., THURMES, W. N. & HALTIWANGER, R. C. (1988). *J. Org. Chem.* **53**, 1046–1056.

Acta Cryst. (1992). **C48**, 1624–1626

Structure of 1,2,3,5,6,7-Hexahydro-1,5:3,7-dimethano-4-benzoxonin-3,5-diol Monohydrate

BY ROGER BISHOP, DONALD C. CRAIG AND MARCIA L. SCUDDER

School of Chemistry, The University of New South Wales, Kensington, New South Wales 2033, Australia

(Received 12 March 1991; accepted 27 January 1992)

Abstract. C₁₄H₁₆O₃·H₂O, *M_r* = 250.30, monoclinic, *P*2₁/*c*, *a* = 10.582 (3), *b* = 6.864 (1), *c* = 17.786 (5) Å, β = 101.84 (1)°, *V* = 1264.4 (6) Å³, *Z* = 4, *D_m* = 1.32,

D_x = 1.31 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.7107 Å (graphite monochromated), μ = 0.89 cm⁻¹, *F*(000) = 536, *T* = 294 K, *R* = 0.040 for 1599 observed [*I*/ σ (*I*) > 3]