

| | | | | |
|----------------|------------|-----------------|------------|---|
| C3—C4—C14 | 114.2 (7) | O4—C18—O5 | 127.3 (9) | Ahmad, V. U., Farooqui, T. A., Sultana, A., Fizza, K. & Khatoon, R. (1992). <i>Phytochemistry</i> , 31 , 2888–2890. |
| C5—C4—C14 | 113.9 (6) | O4—C18—C19 | 109.1 (7) | Ahmad, V. U., Fizza, K. & Amber, A.-Ur-R. (1989). <i>J. Nat. Prod.</i> 52 , 861–863. |
| C4—C5—C6 | 113.9 (5) | O5—C18—C19 | 123.5 (7) | Gilmore, C. J. (1984). <i>J. Appl. Cryst.</i> 17 , 42–46. |
| C4—C5—C10 | 114.9 (6) | O6—C19—C18 | 112.7 (7) | Ivie, R. A., Watson, W. H. & Dominguez, X. A. (1974). <i>Acta Cryst.</i> B30 , 2891–2893. |
| C6—C5—C10 | 111.6 (5) | O6—C19—C20 | 61.5 (6) | Johnson, C. K. (1976). <i>ORTEPII</i> . Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA. |
| C5—C6—C7 | 113.0 (6) | O6—C19—C21 | 113.6 (7) | Molecular Structure Corporation (1985). <i>TEXSAN. TEXRAY Structure Analysis Package</i> . MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA. |
| C6—C7—C8 | 114.4 (7) | C18—C19—C20 | 115.1 (8) | Molecular Structure Corporation (1988). <i>MSC/AFC Diffractometer Control Software</i> . MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA. |
| C6—C7—C11 | 124.0 (7) | C18—C19—C21 | 117.1 (7) | Motherwell, S. & Clegg, W. (1978). <i>PLUTO. Program for Plotting Molecular and Crystal Structures</i> . University of Cambridge, England. |
| C8—C7—C11 | 121.5 (7) | C20—C19—C21 | 123 (1) | Mukhopadhyay, S., Cordell, G. A., Ruangrunsi, N., Rodkird, S., Tantivatana, P. & Hylands, P. J. (1983). <i>J. Nat. Prod.</i> 46 , 671–674. |
| O1—C8—C7 | 122.5 (8) | O6—C20—C19 | 59.6 (5) | Nakanishi, K., Crouch, R., Miura, I., Dominguez, X. A., Zamudio, A. & Villarreal, R. (1974). <i>J. Am. Chem. Soc.</i> 96 , 609–611. |
| O1—C8—C9 | 122.3 (7) | O6—C20—C22 | 114 (1) | North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). <i>Acta Cryst.</i> A24 , 351–359. |
| C7—C8—C9 | 115.2 (6) | C19—C20—C22 | 127 (1) | Spek, A. L. (1990). <i>Acta Cryst.</i> A46 , C-34 |
| C8—C9—C10 | 114.4 (6) | | | Uchiyama, T., Miyase, T., Ueno, A. & Usmanhani, K. (1991). <i>Phytochemistry</i> , 30 , 655–657. |
| O1—C8—C7—C6 | 139.2 (9) | C3—C2—C1—C10 | –56.7 (9) | |
| O1—C8—C7—C11 | –39 (1) | C3—C4—O2—C16 | –58.5 (8) | |
| O1—C8—C9—C10 | –131.2 (8) | C3—C4—C5—C6 | 179.6 (6) | |
| O2—C4—C3—O4 | –37.5 (7) | C3—C4—C5—C10 | 49.1 (8) | |
| O2—C4—C3—C2 | –159.6 (6) | C4—O2—C16—C17 | –176.2 (7) | |
| O2—C4—C5—C6 | –63.0 (6) | C4—C3—O4—C18 | 151.4 (6) | |
| O2—C4—C5—C10 | 166.4 (5) | C4—C5—C6—C7 | 172.9 (6) | |
| O3—C16—O2—C4 | 6 (1) | C4—C5—C10—C9 | –169.2 (6) | |
| O4—C3—C2—C1 | –66.9 (9) | C4—C5—C10—C15 | 71.5 (8) | |
| O4—C3—C4—C5 | 71.3 (6) | C5—C4—O2—C16 | –175.2 (6) | |
| O4—C3—C4—C14 | –158.3 (5) | C5—C6—C7—C8 | 43.9 (9) | |
| O4—C18—C19—O6 | –179.3 (6) | C5—C6—C7—C11 | –138.1 (8) | |
| O4—C18—C19—C20 | –111.3 (8) | C5—C10—C9—C8 | –56.7 (8) | |
| O4—C18—C19—C21 | 46 (1) | C6—C5—C4—C14 | 49.1 (8) | |
| O5—C18—O4—C3 | 7 (1) | C6—C5—C10—C9 | 59.1 (8) | |
| O5—C18—C19—O6 | 3 (1) | C6—C5—C10—C15 | –60.2 (9) | |
| O5—C18—C19—C20 | 71 (1) | C6—C7—C8—C9 | –41 (1) | |
| O5—C18—C19—C21 | –132 (1) | C6—C7—C11—C12 | 180.0 (7) | |
| O6—C19—C20—C22 | 99 (1) | C6—C7—C11—C13 | 3 (1) | |
| O6—C20—C19—C18 | –103.3 (9) | C7—C6—C5—C10 | –54.9 (9) | |
| O6—C20—C19—C21 | 101 (1) | C7—C8—C9—C10 | 49 (1) | |
| C1—C2—C3—C4 | 55 (1) | C8—C7—C11—C12 | –2 (1) | |
| C1—C10—C5—C4 | –50.4 (8) | C8—C7—C11—C13 | –179.4 (8) | |
| C1—C10—C5—C6 | 177.9 (6) | C8—C9—C10—C15 | 66.8 (8) | |
| C1—C10—C9—C8 | –174.6 (6) | C9—C8—C7—C11 | 140.9 (8) | |
| C2—C1—C10—C5 | 54.5 (9) | C10—C5—C4—C14 | –81.5 (7) | |
| C2—C1—C10—C9 | 170.9 (6) | C14—C4—O2—C16 | 66.7 (8) | |
| C2—C1—C10—C15 | –70.9 (8) | C18—C19—O6—C20 | 107.3 (9) | |
| C2—C3—O4—C18 | –83.0 (7) | C18—C19—C20—C22 | –5 (1) | |
| C2—C3—C4—C5 | –50.8 (9) | C19—O6—C20—C22 | –121 (1) | |
| C2—C3—C4—C14 | 79.6 (8) | C20—O6—C19—C21 | –117 (1) | |
| C3—O4—C18—C19 | –170.5 (6) | C21—C19—C20—C22 | –161 (1) | |

All non-H atoms were refined with anisotropic displacement parameters. H atoms were included in the difference Fourier map locations or at calculated positions with isotropic displacement parameters estimated from the displacement parameter of the adjacent C atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *PROCESS TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*; *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *LS TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976); *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *PLATON* (Spek, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1143). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Ahmad, V. U., Farooqui, T. A., Fizza, K., Sultana, A. & Khatoon, R. (1992). *J. Nat. Prod.* **55**, 730–735.

Acta Cryst. (1996). **C52**, 237–244

Structural Aspects of the Nucleophilic Attack of Ketone Enolate on Dehydrodihydropyran

SANDRA IANELLI,^a MARIO NARDELLI,^{a*} DANIELE BELLETTI,^a BRIGITTE JAMART-GRÉGOIRE,^b SOPHIE MERCIER-GIRARDOT^b AND PAUL CAUBÈRE^b

^aDipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università degli Studi di Parma, Centro di Studio per la Strutturistica Diffraattometrica del CNR, Viale delle Scienze 78, I-43100 Parma, Italy, and ^bLaboratoire de Chimie Organique 1, UA CNRS No. 457, Université de Nancy 1, BP 239, 54506 Vandoeuvre-Les-Nancy CEDEX, France

(Received 21 December 1994; accepted 24 July 1995)

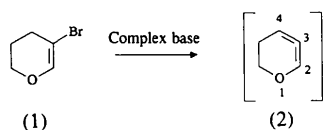
Abstract

The results of the crystal structure analyses of (6*RS*,-7*SR*,8*RS*)-7-methyl-8-phenyl-3-oxabicyclo[4.2.0]oct-1-en-8-ol (C₁₄H₁₆O₂), (1*SR*,2*RS*,8*RS*)-8-methylthio-3-oxatricyclo[6.4.0.0^{2,7}]dodeca-6-en-1-ol (C₁₂H₁₈O₂S) and (1*RS*,2*RS*,6*SR*,7*SR*,8*RS*)-8-methyl-3-oxatricyclo[6.4.0.0^{2,7}]-dodeca-1,6,7-triol (C₁₂H₂₀O₄) allow interpretation of the nucleophilic attack reactions of ketone enolates on the short-lived dehydrodihydropyran intermediate, showing

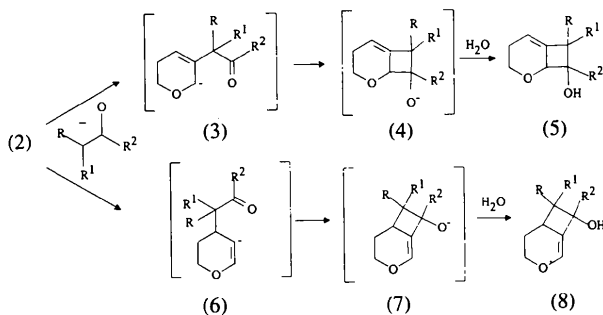
that the presence of the O atom influences the reactivity of the dienic system. The structures and conformations of the above compounds are discussed.

Comment

We have shown previously (Jamart-Grégoire, Grand, Ianelli, Nardelli & Caubère, 1990) that dehydrodihydropyran (2) can easily be generated from 3-bromodihydropyran (1) and a complex base (Caubère, 1978, 1991). In addition, we showed that, under the reaction conditions defined, nucleophiles such as ketone enolates condensed easily with the short-lived intermediate (2).



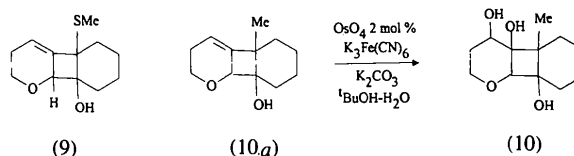
Taking into account the nature of (2), the same type of behaviour as observed for 1,2-cyclohexadienes (Caubère & Brunet, 1972; Brunet, Fixari & Caubère, 1974) could be expected, with nucleophilic attack of the ketone enolate at the C3 position followed by a cyclization of the anionic intermediate. However, the presence of the O atom in the ring could cause some perturbation leading to alternative attacks from the diene system. In reality, depending on the nature of the ketone enolate, attack at the C3 and/or C4 positions was observed, as shown below. Moreover, it was also observed that (4) and (7) could evolve differently to give ketone derivatives (Jamart-Grégoire, Grand, Ianelli, Nardelli & Caubère, 1990).



With respect to the reactions above, the following questions must be answered: What is the stereochemistry of (5) and in particular does it come from a *syn* addition of (2) on the ketone enolate? And, in the absence of information about the reactivity of (2), were the structures attributed to the completely unexpected compound (8) correct and what was their stereochemistry?

The answer to the first question was easily obtained through the usual spectroscopic data as far as the unsubstituted ketone enolates were used (R or $R^1 = H$). Unfortunately, no such information could be obtained

with α -substituted ketones (R and $R^1 \neq H$), so the X-ray crystal structure analysis of compounds (9) and (10) was performed, the latter compound being studied to infer the stereochemistry of the liquid compound (10a).



Regarding the second question, we were lucky enough to obtain single crystals of (8) ($R = CH_3$, $R^2 = Ph$) suitable for X-ray crystal structure analysis.

The results of these structure analyses, illustrated in the present paper, are of interest as they allow definition of the structures of analogous compounds obtained according to the elimination-addition reaction of the scheme above, through comparison of their spectroscopic data. Moreover, they show that the *syn* addition of ketone enolates with the short-lived 1,2-dienes seems to be the rule. More importantly, they definitively establish that nucleophilic attacks on the C4 position of (2) may take place, showing the dramatic influence of the presence of the O atom on the reactivity of the dienic system.

Fig. 1 shows the ORTEP (Johnson, 1965) drawings of the molecules of the three compounds. It should be noted that, while both enantiomeric species are present in the crystals of compounds (9) and (10) as their space groups are centrosymmetric, in the case of compound (8), the two enantiomers do not co-crystallize and only one is present in the crystal. For the crystals of (8), the anomalous-scattering effects were not large enough to allow assignment of the absolute configuration [the value of Flack's (1983) parameter was $x = -0.3$ (4)], so that assigned in Fig. 1 is one of the two possible.

The geometry of the three molecules is described in Tables 2, 4 and 6, respectively, while Table 7 gives the relevant parameters describing the conformation of the three ring systems in the three molecules. The presence of the double bond in the dihydropyran ring of compounds (8) and (9) reduces the tilting of the plane through ring A with respect to that through the central cyclobutane ring B.

The conformation of compound (8) can be deduced from the torsion angles in Table 2, which show that the C1—C8 bond is (–)antiperiplanar to C2—C3, (+)synperiplanar to C7—H7 [C8—C1—C7—H7 = 18(2)°] and (+)antiperiplanar to C7—C14, which is (+)synperiplanar to C1—O1.

In compounds (9) and (10), the system of fused tricycles differs mainly in the presence of the double bond in ring A of compound (9), which causes bond C1—C2 to be (–)synperiplanar to C7—C8 (Table 4), while in compound (10) C1—C2 is (–)antiperiplanar to C7—C8 (Table 6). Another relevant difference in

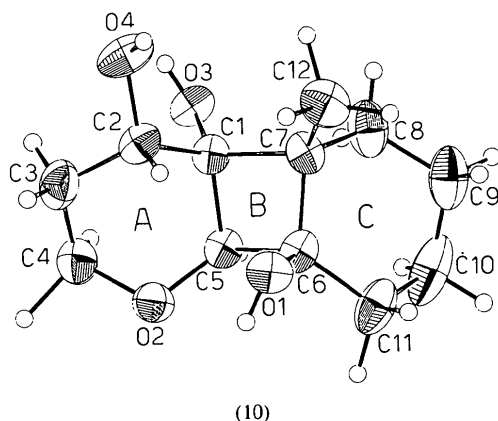
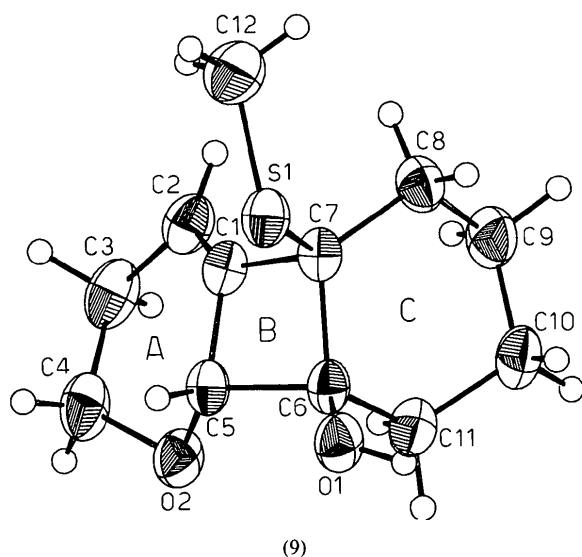
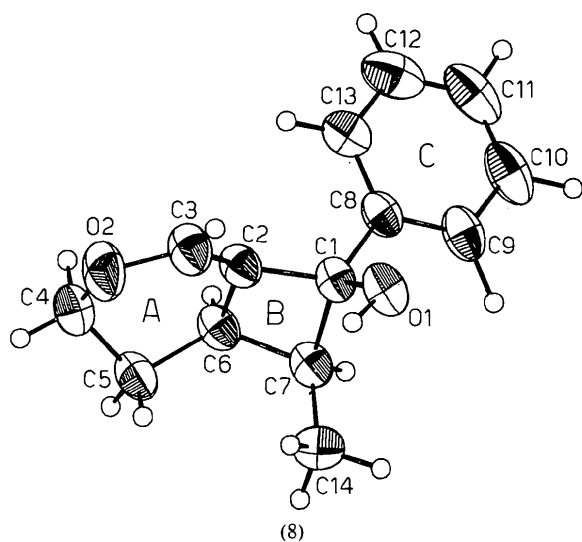


Fig. 1. ORTEP drawings of the molecules of compounds (8), (9) and (10). Ellipsoids are plotted at the 50% probability level.

the conformation of these two systems of fused rings is observed for bond C5—O2 which is (+)synperiplanar to C6—C11 in compound (9) (Table 4) and (+)antiperiplanar in compound (10) (Table 6).

The substituent-carrying side of the cyclobutane ring [C1—C7 for (8), C6—C7 for (9) and (10)] is significantly longer than the other three sides in all three compounds, in agreement with the results of the molecular-mechanics calculations (Tables 2, 4 and 6).

To check the reliability of the structural parameters describing the geometry of the three molecules, particularly for compound (10) whose analysis gave a quite unsatisfactory *R* value (see *Experimental*), and to see how packing forces in the crystal influence the molecular conformation, molecular-mechanics calculations were carried out using both *MMX* and *MM+* force fields of the *PCMODEL* (Serena Software, 1989) and *HYPERCHEM* (Autodesk, Inc., 1992) systems of programs, respectively. In these calculations, isolated molecules were considered and program default parameters were used, starting the energy-minimization process from the molecular structures found experimentally by X-ray diffraction analysis. The results in terms of bond distances, bond angles and torsion angles are compared with those from the experimental analysis in Tables 2, 4 and 6. From this comparison, the following general comments can be made: (i) a rough general evaluation of the disagreement between the experimental and calculated models is given by the averages of the absolute values of the differences $|\Delta|$ (Table 9); (ii) concerning bond distances, negative differences can be justified by the fact that the experimental bond distances are not corrected for thermal motion; (iii) some relevant differences in bond angles are observed when atoms involved in hydrogen bonding or belonging to the cyclobutane ring are considered; (iv) the torsion angles are the parameters showing the largest discrepancies, which can be justified by the packing interactions not considered in the calculated models; (v) it is surprising to find that the lowest differences are observed with compound (10) whose diffraction results, in terms of the *R* index, are the least accurate.

The orientation of the phenyl ring about the C1—C8 bond in compound (8) is defined by the torsion angles about this bond; the differences between the observed and calculated values found for these angles in the isolated molecule (Table 2) are indicative that there is some influence of the packing forces. This finding is in agreement with the non-bonded energy profile, calculated by rotating the phenyl ring about C1—C8 in the isolated molecule, which shows a minimum shifted by *ca* 7° with respect to the position found for the molecule in the crystal. A similar situation is found for the orientation of the methylthio group in the molecule of compound (9), which is defined by the torsion angles about the C7—S1 bond (Table 4). Also in this case, the differences are only a few degrees and the non-bonded

energy profile shows a wide minimum shifted by *ca* 10° with respect to the position found in the crystal.

The orientation of the hydroxyl group in compounds (8) and (9) is determined by the hydrogen bond it forms as a donor towards the pyran O atom and the methylthio S atom of an adjacent molecule, respectively (Table 8). These bonds, together with normal van der Waals interactions, are responsible for the packing in the crystals. In compound (10), the hydroxyls O1—H1O and O3—H3O are both involved, as donor, in intra- and intermolecular bifurcated hydrogen bonds of the type O—H...O, while the O4—H4O hydroxyl group forms only an intermolecular hydrogen bond of this type. Intra- and intermolecular interactions of the type C—H...O, which can be considered as weak hydrogen bonds (Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984), are also observed (Table 8).

The analysis of 'thermal' motion of the molecules in the crystals of the three compounds, carried out in terms of the Schomaker & Trueblood (1968) TLS rigid-body approximation using the *THMV* program (Trueblood, 1984), shows that there are no cases of possible disorder, giving quite satisfactory agreements between the observed and calculated atomic displacement parameters, particularly for compound (9). The overall residual disagreement index *wR_U* is 0.085, 0.055 and 0.094 for (8), (9) and (10), respectively, and these improve to 0.057, 0.039 and 0.067, respectively, if internal motions are considered according to Dunitz & White (1973). These findings for compound (10) are also indicative of the reliability of the results of the diffraction analysis in spite of the inferior value of the *R* index.

Experimental

Compound (8)

Crystal data

C₁₄H₁₆O₂

M_r = 216.28

Orthorhombic

*P*2₁2₁2₁

a = 16.305 (7) Å

b = 10.366 (4) Å

c = 6.900 (4) Å

V = 1166.2 (9) Å³

Z = 4

D_x = 1.232 Mg m⁻³

Data collection

Siemens-AED diffractometer

θ/*2θ* scans

Absorption correction:

none

2508 measured reflections

2209 independent reflections

1821 observed reflections

[*I* > 2σ(*I*)]

R_{int} = 0.0525

Cu Kα radiation

λ = 1.54178 Å

Cell parameters from 30 reflections

θ = 23–40°

μ = 0.644 mm⁻¹

T = 293 (2) K

Tablets

0.36 × 0.29 × 0.21 mm

Colourless

θ_{max} = 70.12°

h = -19 → 19

k = -12 → 0

l = -8 → 0

1 standard reflection

monitored every 50

reflections

intensity variation: within

statistical fluctuation

Refinement

Refinement on *F*²

R(*F*) = 0.0429

wR(*F*²) = 0.0975

S = 1.107

2203 reflections

210 parameters

All H-atom parameters

refined

w = 1/[σ²(*F_o*²) + (0.0539*P*)² + 0.1849*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.214 e Å⁻³

Δρ_{min} = -0.163 e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.107 (5)

Atomic scattering factors

from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8, 6.1.1.4)

Absolute configuration:

Flack (1983)

Flack parameter = -0.3 (4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (8)

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

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U_{eq}</i> |
|-----|------------|------------|-------------|-----------------------|
| O1 | 0.1200 (1) | 0.7085 (2) | 0.1529 (3) | 0.0564 (6) |
| O2 | 0.3118 (1) | 0.5375 (2) | -0.2144 (4) | 0.0750 (8) |
| C1 | 0.1687 (1) | 0.7806 (2) | 0.0209 (3) | 0.0440 (6) |
| C2 | 0.2267 (1) | 0.7074 (2) | -0.1091 (4) | 0.0476 (6) |
| C3 | 0.2376 (2) | 0.5852 (2) | -0.1503 (5) | 0.0617 (9) |
| C4 | 0.3746 (2) | 0.6342 (3) | -0.2406 (5) | 0.0642 (9) |
| C5 | 0.3767 (2) | 0.7320 (3) | -0.0774 (5) | 0.0579 (8) |
| C6 | 0.2952 (1) | 0.8034 (2) | -0.0807 (4) | 0.0475 (7) |
| C7 | 0.2480 (1) | 0.8508 (2) | 0.1023 (4) | 0.0481 (7) |
| C8 | 0.1105 (1) | 0.8727 (2) | -0.0799 (4) | 0.0462 (7) |
| C9 | 0.0708 (1) | 0.9679 (2) | 0.0295 (5) | 0.0587 (8) |
| C10 | 0.0156 (2) | 1.0522 (3) | -0.0601 (6) | 0.0725 (12) |
| C11 | 0.0006 (2) | 1.0429 (3) | -0.2547 (7) | 0.0802 (12) |
| C12 | 0.0396 (2) | 0.9510 (4) | -0.3618 (6) | 0.0802 (13) |
| C13 | 0.0949 (2) | 0.8654 (3) | -0.2763 (4) | 0.0603 (9) |
| C14 | 0.2775 (2) | 0.7986 (3) | 0.2933 (4) | 0.0625 (9) |

Table 2. Comparison of bond distances (Å), bond angles (°) and selected torsion angles (°) in the molecule of compound (8)

E.s.d.'s in parentheses. MMX = force field of *PCMODEL*; MM+ = force field of *HYPERCHEM*; Δ = obs. - calc.

| | X-ray obs. | MMX | | MM+ | |
|----------|------------|-------|--------|-------|--------|
| | | calc. | Δ | calc. | Δ |
| O1—C1 | 1.421 (3) | 1.408 | 0.013 | 1.431 | -0.010 |
| O2—C3 | 1.380 (3) | 1.357 | 0.023 | 1.365 | 0.015 |
| O2—C4 | 1.443 (4) | 1.424 | 0.019 | 1.416 | 0.027 |
| C1—C2 | 1.508 (3) | 1.503 | 0.005 | 1.454 | 0.054 |
| C1—C7 | 1.586 (3) | 1.578 | 0.008 | 1.582 | 0.004 |
| C1—C8 | 1.515 (3) | 1.509 | 0.006 | 1.478 | 0.037 |
| C2—C3 | 1.311 (3) | 1.331 | -0.020 | 1.337 | -0.026 |
| C2—C6 | 1.509 (3) | 1.500 | 0.009 | 1.445 | 0.064 |
| C4—C5 | 1.516 (4) | 1.546 | -0.030 | 1.541 | -0.025 |
| C5—C6 | 1.521 (3) | 1.530 | -0.009 | 1.545 | -0.024 |
| C6—C7 | 1.559 (4) | 1.557 | 0.002 | 1.571 | -0.012 |
| C7—C14 | 1.504 (4) | 1.530 | -0.026 | 1.548 | -0.044 |
| C8—C9 | 1.401 (3) | 1.345 | 0.056 | 1.399 | 0.002 |
| C8—C13 | 1.381 (4) | 1.345 | 0.036 | 1.400 | -0.019 |
| C9—C10 | 1.399 (4) | 1.342 | 0.057 | 1.396 | 0.003 |
| C10—C11 | 1.368 (6) | 1.341 | 0.027 | 1.395 | -0.027 |
| C11—C12 | 1.363 (5) | 1.341 | 0.022 | 1.395 | -0.032 |
| C12—C13 | 1.396 (5) | 1.342 | 0.054 | 1.396 | 0.000 |
| C3—O2—C4 | 114.4 (2) | 121.0 | -6.6 | 116.5 | -2.1 |
| O1—C1—C8 | 106.0 (2) | 113.0 | -7.0 | 112.2 | -6.2 |
| O1—C1—C7 | 118.0 (2) | 113.2 | 4.8 | 114.5 | 3.5 |

| | | | | | |
|--------------|------------|--------|-------|--------|-------|
| O1—C1—C2 | 117.8 (2) | 112.1 | 5.7 | 113.1 | 4.7 |
| C7—C1—C8 | 112.6 (2) | 114.7 | -2.1 | 114.1 | -1.5 |
| C2—C1—C8 | 115.9 (2) | 117.0 | -1.1 | 114.9 | 1.0 |
| C2—C1—C7 | 86.0 (2) | 83.9 | 2.1 | 85.5 | 0.5 |
| C1—C2—C6 | 93.2 (2) | 94.5 | -1.3 | 99.2 | -6.0 |
| C1—C2—C3 | 134.4 (2) | 139.0 | -4.6 | 128.3 | 6.1 |
| C3—C2—C6 | 124.4 (2) | 126.3 | -1.9 | 123.7 | 0.7 |
| O2—C3—C2 | 122.3 (2) | 119.2 | 3.1 | 123.5 | -1.2 |
| O2—C4—C5 | 112.8 (2) | 111.5 | 1.3 | 111.9 | 0.9 |
| C4—C5—C6 | 107.1 (2) | 108.1 | -1.0 | 107.0 | 0.1 |
| C2—C6—C5 | 109.2 (2) | 104.5 | 4.7 | 107.0 | 2.2 |
| C5—C6—C7 | 125.0 (2) | 125.9 | -0.9 | 121.9 | 3.1 |
| C2—C6—C7 | 86.9 (2) | 84.8 | 2.1 | 86.2 | 0.7 |
| C1—C7—C6 | 88.4 (2) | 89.5 | -1.1 | 88.8 | -0.4 |
| C6—C7—C14 | 116.0 (2) | 115.3 | 0.7 | 116.5 | -0.5 |
| C1—C7—C14 | 114.0 (2) | 116.1 | -2.1 | 115.8 | -1.8 |
| C1—C8—C13 | 122.1 (2) | 122.2 | -0.1 | 121.5 | 0.6 |
| C1—C8—C9 | 119.1 (2) | 119.5 | -0.4 | 119.5 | -0.4 |
| C9—C8—C13 | 118.8 (2) | 118.2 | 0.6 | 118.9 | -0.1 |
| C8—C9—C10 | 120.0 (2) | 121.2 | -1.2 | 120.6 | -0.6 |
| C9—C10—C11 | 120.3 (3) | 119.9 | 0.4 | 120.0 | 0.3 |
| C10—C11—C12 | 119.9 (4) | 119.6 | 0.3 | 119.7 | 0.2 |
| C11—C12—C13 | 121.1 (3) | 120.1 | 1.0 | 120.1 | 1.0 |
| C8—C13—C12 | 119.9 (3) | 121.0 | -1.1 | 120.5 | -0.6 |
| O1—C1—C8—C13 | -115.5 (2) | -110.8 | -4.7 | -103.9 | -11.6 |
| O1—C1—C7—C14 | 19.0 (3) | 13.0 | 6.0 | -1.8 | 20.8 |
| O1—C1—C2—C3 | 10.3 (4) | 43.3 | -33.0 | 28.6 | -18.3 |
| C7—C1—C8—C9 | -66.3 (3) | -63.2 | -3.1 | -60.9 | -5.4 |
| C2—C1—C8—C9 | -163.1 (2) | -159.1 | -4.0 | -157.4 | -5.7 |
| C7—C1—C8—C13 | 114.1 (2) | 117.5 | -3.4 | 123.7 | -9.6 |
| C2—C1—C7—C14 | -100.6 (2) | -98.5 | -2.1 | -115.2 | 14.6 |
| C8—C1—C2—C3 | -116.8 (3) | -89.4 | -27.4 | -102.1 | -14.7 |
| C8—C1—C7—C14 | 143.0 (2) | 144.6 | -1.6 | 129.5 | 13.5 |
| C3—C2—C6—C7 | -134.5 (3) | -156.3 | 21.8 | -145.4 | 10.9 |
| C5—C6—C7—C14 | -12.6 (3) | -5.1 | -7.5 | 6.8 | -19.4 |
| C2—C6—C7—C14 | 98.8 (2) | 99.1 | -0.3 | 114.6 | -15.8 |

Distances: $|\Delta|_{\max} \text{MMX} = 0.057 \text{ \AA}$, $\text{MM+} = 0.064 \text{ \AA}$; angles: $|\Delta|_{\max} \text{MMX} = 7.0^\circ$, $\text{MM+} = 6.2^\circ$; torsions: $|\Delta|_{\max} \text{MMX} = 33.0^\circ$, $\text{MM+} = 20.8^\circ$.

Compound (9)

Crystal data

$\text{C}_{12}\text{H}_{18}\text{O}_2\text{S}$

$M_r = 226.33$

Triclinic

$P\bar{1}$

$a = 11.031 (2) \text{ \AA}$

$b = 8.300 (1) \text{ \AA}$

$c = 6.625 (1) \text{ \AA}$

$\alpha = 102.37 (1)^\circ$

$\beta = 93.66 (1)^\circ$

$\gamma = 98.31 (1)^\circ$

$V = 583.4 (2) \text{ \AA}^3$

$Z = 2$

$D_x = 1.288 \text{ Mg m}^{-3}$

Data collection

Siemens AED diffractometer

$\theta/2\theta$ scans

Absorption correction:

none

2231 measured reflections

2218 independent reflections

1913 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0090$

Cu $K\alpha$ radiation

$\lambda = 1.54178 \text{ \AA}$

Cell parameters from 30 reflections

$\theta = 25-39^\circ$

$\mu = 2.240 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Prisms

$0.43 \times 0.33 \times 0.28 \text{ mm}$

Colourless

$\theta_{\max} = 70.24^\circ$

$h = -13 \rightarrow 13$

$k = -10 \rightarrow 9$

$l = -1 \rightarrow 8$

1 standard reflection

monitored every 50

reflections

intensity variation: within statistical fluctuation

Refinement

Refinement on F^2

$R(F) = 0.0322$

$wR(F^2) = 0.0899$

$S = 1.091$

2212 reflections

209 parameters

All H-atom parameters

refined

$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.268 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.323 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0118 (16)

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

[1974, Vol. IV, Tables

2.2A, 2.3.1 (S, O, C),

2.2C (H)]

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (9)

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

| | x | y | z | U_{eq} |
|-----|-------------|-------------|-------------|-----------------|
| S1 | 0.31535 (3) | 0.10498 (4) | 0.31198 (6) | 0.0436 (1) |
| O1 | 0.3930 (1) | -0.0501 (2) | 0.6351 (2) | 0.0469 (4) |
| O2 | 0.09865 (9) | -0.2670 (2) | 0.6173 (2) | 0.0486 (4) |
| C1 | 0.1441 (1) | -0.1730 (2) | 0.3018 (2) | 0.0391 (5) |
| C2 | 0.0430 (2) | -0.2634 (2) | 0.1948 (3) | 0.0479 (5) |
| C3 | -0.0586 (2) | -0.3264 (2) | 0.3156 (3) | 0.0556 (6) |
| C4 | -0.0281 (2) | -0.2668 (3) | 0.5488 (3) | 0.0537 (6) |
| C5 | 0.1712 (1) | -0.1480 (2) | 0.5310 (2) | 0.0386 (5) |
| C6 | 0.3060 (1) | -0.1680 (2) | 0.4906 (2) | 0.0378 (5) |
| C7 | 0.2783 (1) | -0.1235 (2) | 0.2730 (2) | 0.0379 (5) |
| C8 | 0.3337 (2) | -0.2127 (2) | 0.0831 (3) | 0.0477 (6) |
| C9 | 0.3459 (2) | -0.3926 (2) | 0.0896 (3) | 0.0548 (7) |
| C10 | 0.4103 (2) | -0.4007 (2) | 0.2956 (3) | 0.0522 (6) |
| C11 | 0.3305 (2) | -0.3465 (2) | 0.4700 (3) | 0.0469 (6) |
| C12 | 0.2480 (2) | 0.1296 (3) | 0.0686 (4) | 0.0613 (8) |

Table 4. Comparison of bond distances (\AA), bond angles ($^\circ$) and selected torsion angles ($^\circ$) in the molecule of compound (9)

E.s.d.'s in parentheses. MMX = force field of *PCMODEL*; MM+ = force field of *HYPERCHEM*; Δ = obs. - calc.

| | X-ray obs. | MMX | | MM+ | |
|-----------|------------|-------|----------|-------|----------|
| | | calc. | Δ | calc. | Δ |
| S1—C7 | 1.839 (2) | 1.829 | 0.010 | 1.799 | 0.040 |
| S1—C12 | 1.796 (3) | 1.812 | -0.016 | 1.813 | -0.017 |
| O1—C6 | 1.416 (2) | 1.412 | 0.004 | 1.432 | -0.016 |
| O2—C4 | 1.443 (2) | 1.432 | 0.011 | 1.415 | 0.028 |
| O2—C5 | 1.419 (2) | 1.415 | 0.004 | 1.436 | -0.017 |
| C1—C2 | 1.319 (2) | 1.330 | -0.011 | 1.337 | -0.018 |
| C1—C5 | 1.492 (2) | 1.500 | -0.008 | 1.445 | 0.047 |
| C1—C7 | 1.513 (2) | 1.504 | 0.009 | 1.454 | 0.059 |
| C2—C3 | 1.514 (3) | 1.507 | 0.007 | 1.507 | 0.007 |
| C3—C4 | 1.518 (3) | 1.550 | -0.032 | 1.540 | -0.022 |
| C5—C6 | 1.553 (2) | 1.560 | -0.007 | 1.576 | -0.023 |
| C6—C7 | 1.585 (2) | 1.581 | 0.004 | 1.592 | -0.007 |
| C6—C11 | 1.524 (2) | 1.536 | -0.012 | 1.555 | -0.031 |
| C7—C8 | 1.528 (2) | 1.531 | -0.003 | 1.553 | -0.025 |
| C8—C9 | 1.528 (3) | 1.532 | -0.004 | 1.532 | -0.004 |
| C9—C10 | 1.517 (3) | 1.533 | -0.016 | 1.531 | -0.014 |
| C10—C11 | 1.528 (3) | 1.531 | -0.003 | 1.529 | -0.001 |
| C7—S1—C12 | 99.7 (1) | 100.8 | -1.1 | 98.4 | 1.3 |
| C4—O2—C5 | 106.8 (1) | 108.3 | -1.5 | 108.9 | -2.1 |
| C5—C1—C7 | 92.3 (1) | 94.3 | -2.0 | 99.1 | -6.8 |
| C2—C1—C7 | 139.3 (1) | 139.2 | 0.1 | 130.5 | 8.8 |
| C2—C1—C5 | 124.1 (1) | 126.3 | -2.2 | 124.4 | -0.3 |
| C1—C2—C3 | 117.6 (1) | 116.3 | 1.3 | 118.4 | -0.8 |
| C2—C3—C4 | 112.8 (2) | 113.5 | -0.7 | 112.2 | 0.6 |

| | | | | | |
|--------------|------------|--------|------|--------|-------|
| O2—C4—C3 | 113.5 (1) | 112.6 | 0.9 | 110.9 | 2.6 |
| O2—C5—C1 | 113.8 (1) | 108.0 | 5.8 | 110.8 | 3.0 |
| C1—C5—C6 | 87.3 (1) | 83.9 | 3.4 | 85.5 | 1.8 |
| O2—C5—C6 | 119.6 (1) | 120.2 | -0.6 | 119.3 | 0.3 |
| O1—C6—C5 | 112.4 (1) | 110.7 | 1.7 | 112.5 | -0.1 |
| C5—C6—C11 | 113.3 (1) | 114.6 | -1.3 | 112.3 | 1.0 |
| C5—C6—C7 | 87.3 (1) | 89.0 | -1.7 | 88.3 | -1.0 |
| O1—C6—C11 | 112.6 (1) | 110.9 | 1.7 | 111.2 | 1.4 |
| O1—C6—C7 | 116.1 (1) | 112.9 | 3.2 | 113.6 | 2.5 |
| C7—C6—C11 | 112.8 (1) | 117.1 | -4.3 | 117.2 | -4.4 |
| C1—C7—C6 | 85.5 (1) | 83.0 | 2.5 | 84.6 | 0.9 |
| S1—C7—C6 | 107.4 (1) | 114.0 | -6.6 | 112.0 | -4.6 |
| S1—C7—C1 | 109.8 (1) | 110.2 | -0.4 | 109.7 | 0.1 |
| C6—C7—C8 | 119.4 (1) | 116.4 | 3.0 | 116.4 | 3.0 |
| C1—C7—C8 | 120.4 (1) | 117.4 | 3.0 | 117.9 | 2.5 |
| S1—C7—C8 | 111.4 (1) | 112.6 | -1.2 | 113.1 | -1.7 |
| C7—C8—C9 | 112.5 (1) | 115.0 | -2.5 | 114.7 | -2.2 |
| C8—C9—C10 | 111.1 (2) | 110.4 | 0.7 | 109.4 | 1.7 |
| C9—C10—C11 | 109.5 (2) | 108.7 | 0.8 | 108.2 | 1.3 |
| C6—C11—C10 | 113.2 (1) | 111.7 | 1.5 | 112.9 | 0.3 |
| C12—S1—C7—C1 | -76.9 (1) | -73.0 | -3.9 | -70.8 | -6.1 |
| C12—S1—C7—C6 | -168.4 (1) | -164.3 | -4.1 | -163.0 | -5.4 |
| C12—S1—C7—C8 | 59.0 (1) | 60.2 | -1.2 | 63.0 | -4.0 |
| C4—O2—C5—C6 | -153.5 (1) | -154.4 | 0.9 | -154.9 | 1.4 |
| C2—C1—C7—S1 | 119.1 (2) | 95.7 | 23.4 | 108.2 | 10.9 |
| C2—C1—C7—C8 | -12.3 (3) | -35.1 | 22.8 | -23.2 | 10.9 |
| C5—C1—C2—C3 | 8.3 (3) | -3.0 | 11.3 | 4.2 | 4.1 |
| O2—C5—C6—O1 | -106.7 (2) | -115.6 | 8.9 | -122.5 | 15.8 |
| O2—C5—C6—C7 | 136.2 (1) | 130.2 | 6.0 | 122.7 | 13.5 |
| O2—C5—C6—C11 | 22.4 (2) | 10.7 | 11.7 | 3.9 | 18.5 |
| O1—C6—C7—S1 | -24.4 (2) | -25.8 | 1.4 | -15.9 | -8.5 |
| O1—C6—C7—C8 | 103.8 (2) | 107.9 | -4.1 | 116.4 | -12.6 |

Distances: $|\Delta|_{\max}$ MMX = 0.032 Å, MM+ = 0.059 Å; angles: $|\Delta|_{\max}$ MMX = 6.6°, MM+ = 8.8°; torsions: $|\Delta|_{\max}$ MMX = 23.4°, MM+ = 18.5°.

Compound (10)

Crystal data

C₁₂H₂₀O₄
M_r = 228.29
 Orthorhombic
*Pc*61 (No. 61)
a = 18.992 (7) Å
b = 10.595 (3) Å
c = 11.875 (5) Å
V = 2389 (2) Å³
Z = 8
D_x = 1.269 Mg m⁻³

Data collection

Siemens AED diffractometer
 $\theta/2\theta$ scans
 Absorption correction:
 none
 4462 measured reflections
 2277 independent reflections
 2001 observed reflections
 $[I > 2\sigma(I)]$
R_{int} = 0.0462

Refinement

Refinement on *F*²
R(*F*) = 0.1071
wR(*F*²) = 0.2100
S = 1.265
 2277 reflections

Cu Kα radiation
 λ = 1.54178 Å
 Cell parameters from 30 reflections
 θ = 24–40°
 μ = 0.773 mm⁻¹
T = 293 (2) K
 Thin tablets
 0.41 × 0.33 × 0.16 mm
 Colourless

θ_{\max} = 70.20°
 h = -23 → 23
 k = -1 → 12
 l = 0 → 14
 1 standard reflection
 monitored every 50 reflections
 intensity variation: within statistical fluctuation

$\Delta\rho_{\max}$ = 0.241 e Å⁻³
 $\Delta\rho_{\min}$ = -0.211 e Å⁻³
 Extinction correction:
 SHELXL93 (Sheldrick, 1993)

226 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 3.1057P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

Extinction coefficient:
 0.001 (0)
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8, 6.1.1.4)

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (10)

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

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U_{eq}</i> |
|-----|------------|------------|-------------|-----------------------|
| O1 | 0.8452 (2) | 0.3368 (3) | 0.2736 (3) | 0.0510 (10) |
| O2 | 0.7566 (2) | 0.1306 (3) | 0.2805 (3) | 0.0548 (10) |
| O3 | 0.7777 (2) | 0.1020 (2) | 0.0008 (3) | 0.0477 (9) |
| O4 | 0.7127 (2) | 0.3367 (3) | -0.0062 (3) | 0.0675 (12) |
| C1 | 0.7935 (2) | 0.1927 (3) | 0.0859 (4) | 0.0405 (12) |
| C2 | 0.7316 (2) | 0.2823 (4) | 0.1002 (4) | 0.0498 (14) |
| C3 | 0.6690 (3) | 0.2078 (6) | 0.1485 (5) | 0.0682 (19) |
| C4 | 0.6910 (3) | 0.1015 (6) | 0.2268 (5) | 0.0686 (19) |
| C5 | 0.8110 (2) | 0.1319 (4) | 0.1988 (4) | 0.0425 (14) |
| C6 | 0.8709 (2) | 0.2279 (3) | 0.2166 (4) | 0.0456 (14) |
| C7 | 0.8695 (2) | 0.2512 (4) | 0.0865 (4) | 0.0471 (13) |
| C8 | 0.9225 (3) | 0.1642 (6) | 0.0254 (6) | 0.072 (2) |
| C9 | 0.9926 (3) | 0.1591 (7) | 0.0821 (7) | 0.084 (3) |
| C10 | 0.9848 (3) | 0.1018 (6) | 0.1970 (8) | 0.093 (3) |
| C11 | 0.9396 (3) | 0.1854 (5) | 0.2726 (6) | 0.0689 (19) |
| C12 | 0.8796 (4) | 0.3867 (5) | 0.0478 (6) | 0.071 (20) |

Table 6. Comparison of bond distances (Å), bond angles (°) and selected torsion angles (°) in the molecule of compound (10)

E.s.d.'s in parentheses. MMX = force field of PCMODEL; MM+ = force field of HYPERCHEM; Δ = obs. – calc.

| | X-ray obs. | MMX | | MM+ | |
|----------|------------|-------|--------|-------|--------|
| | | calc. | Δ | calc. | Δ |
| O1—C6 | 1.424 (5) | 1.414 | 0.010 | 1.436 | -0.012 |
| O2—C4 | 1.432 (6) | 1.422 | 0.010 | 1.411 | 0.021 |
| O2—C5 | 1.418 (5) | 1.418 | 0.000 | 1.437 | -0.019 |
| O3—C1 | 1.427 (5) | 1.412 | 0.015 | 1.431 | -0.004 |
| O4—C2 | 1.434 (6) | 1.414 | 0.020 | 1.404 | 0.030 |
| C1—C2 | 1.519 (6) | 1.533 | -0.014 | 1.547 | -0.028 |
| C1—C5 | 1.524 (6) | 1.553 | -0.029 | 1.562 | -0.038 |
| C1—C7 | 1.571 (6) | 1.563 | 0.008 | 1.577 | -0.006 |
| C2—C3 | 1.538 (7) | 1.539 | -0.001 | 1.536 | 0.002 |
| C3—C4 | 1.519 (9) | 1.542 | -0.023 | 1.540 | -0.021 |
| C5—C6 | 1.541 (6) | 1.552 | -0.011 | 1.561 | -0.020 |
| C6—C7 | 1.565 (6) | 1.562 | 0.003 | 1.574 | -0.009 |
| C6—C11 | 1.531 (7) | 1.531 | 0.000 | 1.547 | -0.016 |
| C7—C8 | 1.546 (7) | 1.545 | 0.001 | 1.561 | -0.015 |
| C7—C12 | 1.520 (7) | 1.533 | -0.013 | 1.551 | -0.031 |
| C8—C9 | 1.494 (8) | 1.532 | -0.038 | 1.531 | -0.037 |
| C9—C10 | 1.501 (12) | 1.534 | -0.033 | 1.533 | -0.032 |
| C10—C11 | 1.525 (10) | 1.530 | -0.005 | 1.530 | -0.005 |
| C4—O2—C5 | 109.4 (3) | 110.1 | -0.7 | 109.8 | -0.4 |
| O3—C1—C2 | 109.7 (3) | 109.6 | 0.1 | 110.7 | -1.0 |
| O3—C1—C5 | 112.6 (3) | 110.4 | 2.2 | 112.7 | -0.1 |
| O3—C1—C7 | 117.5 (3) | 114.4 | 3.1 | 115.7 | 1.8 |
| C2—C1—C5 | 109.6 (3) | 110.5 | -0.9 | 108.4 | 1.2 |
| C2—C1—C7 | 117.6 (3) | 121.6 | -4.0 | 117.9 | -0.3 |
| C5—C1—C7 | 87.8 (3) | 88.0 | -0.2 | 89.4 | -1.6 |
| O4—C2—C1 | 110.3 (3) | 110.3 | 0.0 | 111.3 | -1.0 |
| O4—C2—C3 | 109.9 (4) | 110.4 | -0.5 | 109.6 | 0.3 |
| C3—C2—C1 | 108.6 (4) | 108.7 | -0.1 | 108.9 | -0.3 |
| C2—C3—C4 | 113.3 (5) | 111.8 | 1.5 | 111.7 | 1.6 |
| O2—C4—C3 | 110.7 (4) | 110.8 | -0.1 | 110.8 | -0.1 |
| C2—C5—C1 | 116.5 (3) | 113.1 | 3.4 | 113.6 | 2.9 |
| O2—C5—C6 | 116.8 (3) | 113.7 | 3.1 | 114.0 | 2.8 |
| C1—C5—C6 | 90.2 (3) | 88.3 | 1.9 | 89.2 | 1.0 |
| O1—C6—C5 | 110.3 (3) | 110.8 | -0.5 | 109.2 | 1.1 |
| O1—C6—C7 | 109.6 (3) | 111.3 | -1.7 | 111.7 | -2.1 |

| | | | | | |
|--------------|------------|--------|-------|--------|-------|
| O1—C6—C11 | 108.9 (3) | 108.6 | 0.3 | 109.3 | -0.4 |
| C5—C6—C7 | 87.4 (3) | 88.1 | -0.7 | 89.6 | -2.2 |
| C5—C6—C11 | 119.6 (4) | 117.9 | 1.7 | 117.2 | 2.4 |
| C7—C6—C11 | 119.3 (4) | 118.8 | 0.5 | 118.5 | 0.8 |
| C1—C7—C6 | 87.6 (3) | 87.6 | 0.0 | 88.2 | -0.6 |
| C1—C7—C8 | 111.2 (3) | 113.5 | -2.3 | 111.0 | 0.2 |
| C1—C7—C12 | 119.2 (4) | 115.4 | 3.8 | 116.9 | 2.3 |
| C6—C7—C8 | 111.0 (4) | 112.7 | -1.7 | 114.0 | -3.0 |
| C6—C7—C12 | 116.4 (4) | 115.2 | 1.2 | 114.4 | 2.0 |
| C8—C7—C12 | 109.8 (4) | 110.7 | -0.9 | 110.7 | -0.9 |
| C7—C8—C9 | 113.0 (4) | 113.1 | -0.1 | 112.9 | 0.1 |
| C8—C9—C10 | 109.6 (6) | 108.7 | 0.9 | 108.4 | 1.2 |
| C9—C10—C11 | 110.9 (6) | 109.7 | 1.2 | 109.5 | 1.4 |
| C6—C11—C10 | 113.2 (4) | 115.1 | -1.9 | 114.6 | -1.4 |
| C4—O2—C5—C1 | 40.8 (5) | 52.5 | -11.7 | 50.1 | -9.3 |
| C4—O2—C5—C6 | 145.6 (4) | 148.9 | -3.3 | 152.8 | -7.2 |
| O3—C1—C2—O4 | -53.7 (4) | -55.8 | 2.1 | -54.1 | 0.4 |
| O3—C1—C5—O2 | -100.8 (4) | -108.4 | 7.6 | -112.1 | 11.3 |
| O3—C1—C7—C8 | -22.5 (5) | -18.8 | -3.7 | -14.0 | -8.5 |
| C2—C1—C7—C12 | -27.8 (6) | -24.9 | -2.9 | -20.0 | -7.8 |
| O4—C2—C3—C4 | 153.3 (4) | 160.2 | -6.9 | 165.7 | -12.4 |
| O2—C5—C6—O1 | -30.1 (5) | -16.9 | -13.2 | -23.7 | -6.4 |
| O2—C5—C6—C11 | 97.3 (5) | 102.3 | -5.0 | 108.0 | -10.7 |
| C1—C5—C6—O1 | 89.9 (3) | 90.9 | -1.0 | 98.7 | -8.8 |
| O1—C6—C7—C1 | -91.2 (3) | -90.6 | -0.6 | -96.6 | 5.4 |
| O1—C6—C7—C12 | 30.4 (5) | 26.5 | 3.9 | 22.3 | 8.1 |
| C5—C6—C7—C8 | -92.3 (4) | -93.6 | 1.3 | -98.3 | 6.0 |

Distances: $|\Delta|_{\max} MMX = 0.038 \text{ \AA}$, $MM+ = 0.038 \text{ \AA}$; angles: $|\Delta|_{\max} MMX = 3.8^\circ$, $MM+ = 3.0^\circ$; torsions: $|\Delta|_{\max} MMX = 9.3^\circ$, $MM+ = 13.2^\circ$.

Table 7. Conformation of the rings and dihedral angles ($^\circ$) of ring planes

Q_T = total puckering amplitude (\AA) (Cremer & Pople, 1975), DAP = minimum displacement asymmetry parameter (Nardelli, 1983b), HC = half chair, S = sofa, T = twist.

| Ring | Q_T | DAP | Conformation | A/B | B/C | A/C |
|---------------|-------------|---|--------------|-----------|-----------|-----------|
| Compound (8) | | | | | | |
| A | 0.522 (3) | $D2(C3-C2) = 0.024$ (1) | HC | | | |
| B | -0.0615 (6) | | | 151.8 (1) | 110.6 (1) | 107.3 (1) |
| C | 0.007 (2) | | | | | |
| Compound (9) | | | | | | |
| A | 0.508 (2) | $D2(C1-C2) = 0.0546$ (8) | HC | | | |
| B | -0.0720 (5) | | | 154.4 (1) | 118.4 (1) | 92.8 (1) |
| C | 0.523 (2) | $DS(C7) = 0.040$ (2) $D2(C6-C7) = 0.037$ (1) | S/HC | | | |
| Compound (10) | | | | | | |
| A | 0.749 (4) | $D2(C4-O2) = 0.042$ (2) $D2(C3) = 0.032$ (1) | T | | | |
| B | 0.070 (1) | | | 135.2 (2) | 117.7 (2) | 149.7 (2) |
| C | 0.524 (6) | $DS(C6) = 0.013$ (3) $D2(C6-C11) = 0.073$ (2) $D2(C7-C6) = 0.055$ (2) | S/T | | | |

Table 8. Hydrogen-bonding geometry (\AA , $^\circ$)

| D—H...A | D—H | H...A | D...A | D—H...A |
|----------------------------|----------|----------|-----------|---------|
| Compound (8) | | | | |
| O1—H10...O2 ⁱ | 0.88 (3) | 2.11 (3) | 2.929 (3) | 154 (3) |
| Compound (9) | | | | |
| O1—H10...S1 ⁱⁱ | 0.83 (3) | 2.51 (3) | 3.321 (1) | 164 (2) |
| Compound (10) | | | | |
| O1—H10...O2 | 0.86 (6) | 2.45 (5) | 2.759 (4) | 101 (4) |
| O3—H3O...O4 | 0.81 (6) | 2.38 (6) | 2.778 (4) | 111 (5) |
| C2—H2...O1 | 0.99 (4) | 2.33 (4) | 3.037 (6) | 128 (3) |
| O1—H10...O4 ⁱⁱⁱ | 0.86 (6) | 2.04 (6) | 2.838 (5) | 153 (5) |
| O3—H3O...O2 ^{iv} | 0.81 (6) | 2.04 (6) | 2.713 (4) | 140 (6) |
| O4—H4O...O3 ^v | 0.83 (9) | 2.02 (9) | 2.817 (4) | 160 (9) |
| C5—H5...O1 ^{vi} | 0.92 (5) | 2.35 (5) | 3.209 (5) | 155 (4) |

Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (ii) $1 - x, -y, 1 - z$; (iii) $\frac{1}{2} - x, y, \frac{1}{2} + z$; (iv) $\frac{1}{2} - x, y, z - \frac{1}{2}$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, -z$; (vi) $x, y - \frac{1}{2}, \frac{1}{2} - z$.

Table 9. Averages of the absolute differences $|\Delta|$

| Distances (\AA) | $ \Delta _{MMX}$ | (8) | (9) | (10) | | | |
|----------------------------|------------------|-------|-------|-------|-------|-------|-------|
| | | Ave* | Ave* | Ave* | Ave* | | |
| | $ \Delta _{MMX}$ | 0.023 | 0.031 | 0.009 | 0.017 | 0.019 | 0.011 |
| | $ \Delta _{MM+}$ | 0.024 | | 0.022 | | 0.013 | |
| Angles ($^\circ$) | $ \Delta _{MMX}$ | 2.2 | 1.8 | 2.1 | 1.6 | 1.2 | 0.9 |
| | $ \Delta _{MM+}$ | 1.7 | | 2.1 | | 1.3 | |
| Torsions ($^\circ$) | $ \Delta _{MMX}$ | 14.2 | 10.8 | 5.1 | 6.5 | 6.4 | 4.8 |
| | $ \Delta _{MM+}$ | 10.3 | | 7.8 | | 2.7 | |

* Ave = $\Delta(|MMX| - |MM+|)$.

The integrated intensities were obtained by a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. All reflections of the three compounds were corrected for Lorentz and polarization effects but not for absorption.

The three structures were solved by direct methods and refined by anisotropic full-matrix least squares. In all three cases, the H atoms were found from $\Delta\rho$ maps and refined isotropically. The crystals of compound (10) were of poor quality so the R index is not as good as for the other two compounds. Nevertheless, refinement proceeded smoothly for (10) (comprehensive of H atoms) giving a quite acceptable molecular geometry and anisotropic displacement parameters (see Tables 5–8 and *Comment*). Calculations were carried out on the ENCORE91 and GOULD-POWERNODE 6040 computers of the Centro di Studio per la Strutturistica Diffraattometrica del CNR (Parma), and on a COMPAQ-486c portable computer.

For all compounds, data collection: local programs; cell refinement: *LQPARM* (Nardelli & Mangia, 1984); data reduction: local programs. Program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990) for (8) and (9); *SIR92* (Altomare *et al.* 1994) for (10). For all compounds, program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *PARST* (Nardelli, 1983a); *PARSTCIF* (Nardelli, 1991).

Financial support from the European Community Commission under contract N.SC1000657 is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1044). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

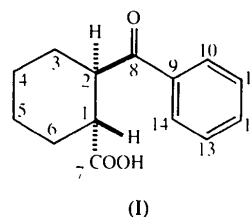
References

- Altomare, A., Cascarano, O., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.
- Autodesk, Inc. (1992). *HYPERCHEM*. Version 2.0. Autodesk, Inc., 2320 Marinship Way, San Ramon, CA 94565, USA.
- Belletti, D., Ugozzoli, F., Cantoni, A. & Pasquinelli, G. (1979). *Gestione on Line di Diffratometro a Cristallo Singolo Siemens AED con Sistema General Automation Jumbo 220*. Internal Reports 1–3/79. Centro di Studio per la Strutturistica Diffraattometrica del CNR, Parma, Italy.
- Berkovitch-Yellin, L. & Leiserowitz, L. (1984). *Acta Cryst.* **B40**, 159–165.

- Brunet, J. J., Fixari, B. & Caubère, P. (1974). *Tetrahedron*, **30**, 1237–1243.
- Caubère, P. (1978). *Top. Curr. Chem.* **73**, 48–124.
- Caubère, P. (1991). *Rev. Heteroatom. Chem.* **4**, 78–139.
- Caubère, P. & Brunet, J. J. (1972). *Tetrahedron*, **28**, 4835–4845.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Dunitz, J. D. & White, D. N. J. (1973). *Acta Cryst.* **A29**, 93–94.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Jamart-Grégoire, B., Grand, V., Ianelli, S., Nardelli, M. & Caubère, P. (1990). *Tetrahedron Lett.* pp. 7603–7606.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* **A30**, 580–589.
- Nardelli, M. (1983a). *Comput. Chem.* **7**, 95–98.
- Nardelli, M. (1983b). *Acta Cryst.* **C39**, 1141–1142.
- Nardelli, M. (1991). *PARSTCIF. Program for the Creation of a CIF from the Output of PARST*. University of Parma, Italy.
- Nardelli, M. & Mangia, A. (1984). *Ann. Chim. (Rome)*, **74**, 163–174.
- Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- Serena Software. (1989). *PCMODEL*. Version 4.0. Serena Software, Bloomington, IN 47402-3076, USA.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
- Trueblood, K. N. (1984). *THMV. Program for Thermal Motion Analysis*. University of California, Los Angeles, USA.

ular carboxyl-to-ketone hydrogen bonds repeat infinitely along one cell axis to yield a chain or catemer. A third rare arrangement is an internal hydrogen bond and one instance is known of acid-to-ketone dimerization. We have previously referenced and discussed many examples of these (Thompson, Lalancette & Vanderhoff, 1992; Coté, Thompson & Lalancette, 1996).

γ -Keto acids constitute a class particularly rich in hydrogen-bonding types, with examples of dimers, internal hydrogen bonds and catemers of both the helical and translational type. Despite the expectation of an intramolecular hydrogen bond for the *cis* counterpart of the title compound (Pourahmady & Eisenbraun, 1982), it was found to crystallize as a centrosymmetric dimer (Choney, Holt, Pourahmady & Eisenbraun, 1983). We report here that the *trans* epimer, (I), also adopts



the common carboxylic acid dimer motif, but that the dimer components are crystallographically unrelated, leading to an unusually long cell dimension [40.748 (6) Å] for such a small molecule (17 non-H atoms).

Friedel–Crafts acylation of benzene with *cis*-1,2-cyclohexanedicarboxylic anhydride yields, as the immediate product, the less stable *cis*-keto acid (m.p. 413 K). Aqueous base epimerizes this to the more stable *trans* diastereomer (m.p. 427 K) (Scribner & Miller, 1965).

Fig. 1 presents a view of the asymmetric unit with its numbering scheme. The cell contains four asymmetric units ($Z = 8$), each consisting of a pair of conformationally distinct molecules of opposite chirality, reciprocally hydrogen bonded through their carboxyl groups, with no ketone participation in the hydrogen bonding. Each molecule, as expected, has its substituents equatorial to a chair cyclohexane and the two molecules in the asymmetric unit differ almost entirely in the rotational orientation of the benzene ring. The carboxyl group adopts a conformation relative to its ring H atom whose torsion angle is 31.9° for molecule *A* and 30.1° for molecule *B*. The torsion angle for the benzoyl C=O relative to its axial ring H atom is 138.9° for molecule *A* and 141.0° for molecule *B*. Hence, the dihedral angles between the ketone and carboxyl planes are nearly identical in the two molecules, 73.0° in *A* and 70.2° in *B*. In molecule *A*, however, the dihedral angle of the aromatic ring relative to the ketone is 31.9°, whereas this angle is 9.7° in molecule *B*.

The carboxyl C—O bond lengths and C—C—O angles are found to be only slightly disordered, although

Acta Cryst. (1996). **C52**, 244–246

(±)-*trans*-2-Benzoylcyclohexanecarboxylic Acid. Structure and Hydrogen-Bonding Pattern of a γ -Keto Acid

ROGER A. LALANCETTE, MARIE L. COTÉ AND HUGH W. THOMPSON

Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, NJ 07102, USA

(Received 16 August 1994; accepted 25 July 1995)

Abstract

In the title compound, C₁₄H₁₆O₃, enantiomeric pairs of molecules form dimers by mutual hydrogen bonding of carboxyl groups, with the ketone group not involved in the hydrogen bonding. The components of the dimer differ in conformation, so that the dimer is the asymmetric unit.

Comment

Our interest in simple keto carboxylic acids arises from their four known crystalline hydrogen-bonding states. The commonest retains the dimer pattern characteristic of almost all functionally unelaborated acids in which the ketone is not involved. Less commonly, intermolec-