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References

Anderson, G. P. (1993). *Life Sci.* **52**, 2145–2160.

Faulds, D., Hollingshead, L. M. & Goa, K. L. (1991). *Drugs*, **42**, 115–137.

Ida, H. (1976*a*). *Arzneim. Forsch.* **26**, 839–842.

Ida, H. (1976*b*). *Arzneim. Forsch.* **26**, 1337–1340.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Klyne, W. & Buckingham, J. (1978). In *Atlas of Stereochemistry, Absolute Configurations of Organic Molecules*, 2nd ed. London: Chapman & Hall.

Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software*. Version 4.3.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Murase, K., Mase, T., Ida, H. & Takahashi, K. (1977). *Chem. Pharm. Bull.* **25**, 1368–1377.

Murase, K., Mase, T., Ida, H., Takahashi, K. & Murakami, M. (1978). *Chem. Pharm. Bull.* **26**, 1123–1129.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.

Tattersfield, A. E. (1993). *Life Sci.* **52**, 2161–2169.

Acta Cryst. (1997). C**53**, 1889–1892

Three 2,5-Disubstituted 9-Oxabicyclo[4.2.1]-nonanes. Transannular O-Heterocyclization Products of Cycloocta-1,5-diene

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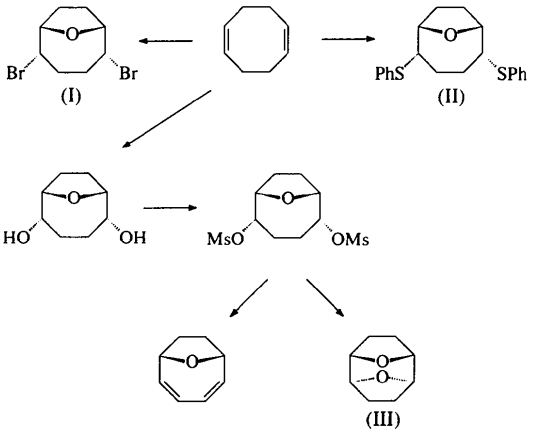
Abstract

The crystal structures of *endo,endo*-2,5-dibromo-9-oxabicyclo[4.2.1]nonane, (I), $C_8H_{12}Br_2O$, *endo,endo*-2,5-bis-(phenylthio)-9-oxabicyclo[4.2.1]nonane, (II), $C_{20}H_{22}OS_2$, and 9,10-dioxatricyclo[4.2.1.$1^{2,5}$]decane, (III), $C_8H_{12}O_2$, were determined and the conformations of these transannular O-heterocyclization products of cycloocta-1,5-diene were defined. The structure determinations reveal a tetrahydrofuran ring having an envelope conformation and an oxepane ring with a twisted-chair conformation in each of (I) and (II), with the two bulky substituents quasi-equatorial or quasi-axial, respectively, both in a *trans* position in relation to the ring O atom. The tricyclic compound (III) consists of two five-membered envelopes and a 1,4-dioxane chair. The cyclooctane moiety has a twisted-chair conformation in both (I) and (II), whereas it is a chair in (III).

Comment

Transannular O-heterocyclization of cycloocta-1,5-diene represents the easiest way to obtain disubstituted bicyclic ethers, by employing an electrophilic cascade reaction. These compounds have been designed as starting materials for syntheses of natural products and their analogues. In consecutive reactions, the conformation seems to be very important. Therefore, we determined the structures of the polycyclic tetrahydrofurans (I), (II) and (III).



Among natural products, polycycles having a tetrahydrofuran moiety are very common, especially in marine diterpenoids (Wahlberg & Eklund, 1992; Faulkner, 1996). However, no crystalline-state structures of simple synthetic building blocks for such compounds have been reported in the literature. *endo,endo*-2,5-Dibromo-9-oxabicyclo[4.2.1]nonane, (I), can be prepared using *N*-bromosuccinimide and dioxane/water (4:1) as a solvent (Haufe, 1984). The conformation in solution of (I) and the *endo*-2-bromo-*endo*-5-fluoro analogue had been assumed earlier (Kleinpeter *et al.*, 1977; Haufe *et al.*, 1978; Haufe, Alvernhe & Laurent, 1990). Based on ^{1}H NMR spectra, an envelope conformation was predicted for the five-membered ring and a chair conformation for the oxaheptane moiety. This assignment is now established by X-ray structure analysis. The same conformation is observed for *endo,endo*-2,5-bis(phenylsulfenyl)-9-oxabicyclo[4.2.1]nonane, (II). Due to the symmetry of the space group, the asymmetric unit contains only one half of the molecule. The second half

is generated by a mirror plane, symmetry-related by (x, $-y+\frac{3}{2}$, z). Additionally, (II) shows disorder in the C3—C4—C4*—C3* bridge. Refinement led to an occupancy of 50% for each of positions C4*A* and C4*B*.

In order to prepare 9-oxabicyclo[4.2.1]nona-2,4-diene, an interesting 1,3-diene (Cope, McKervey & Weinshenker, 1969), using *endo,endo*-2,5-dihydroxy-9-oxabicyclo[4.2.1]nonane as a precursor (Lafont & Vivant, 1963; Eaton & Millikan, 1990), we proceeded according to the scheme depicted above. The tricyclic system 9,10-dioxatricyclo[4.2.1.$1^{2,5}$]decane, (III), was obtained as a by-product. Molecule (III) has a very rigid conformation of two envelopes and two chairs. As in (II), the asymmetric unit of (III) contains only half of the molecule. The second half is generated by an inversion centre at ($-x$, $-y+2$, $-z+1$).

In all three structures, no intermolecular contacts are shorter than normal van der Waals separations.

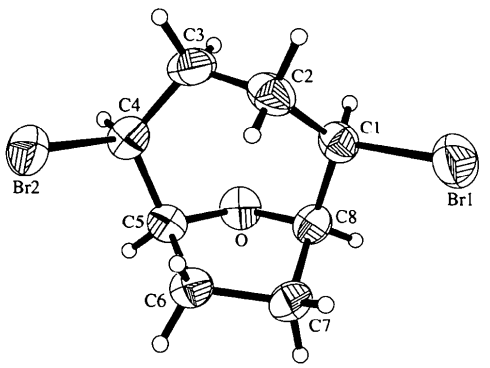


Fig. 1. *XP* (Siemens, 1990) plot of compound (I) with the atomic numbering scheme (50% probability ellipsoids).

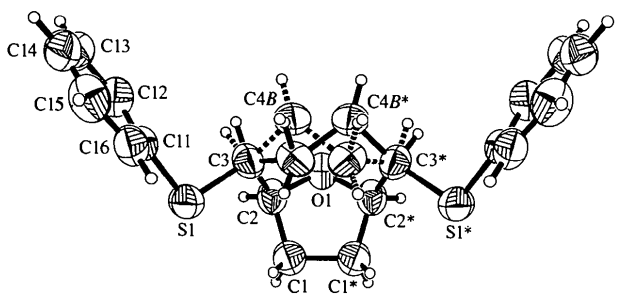


Fig. 2. *XP* (Siemens, 1990) plot of compound (II) with the atomic numbering scheme (50% probability ellipsoids). Atoms marked with an asterisk (*) are in the symmetry position ($-x, 2-y, 1-z$).

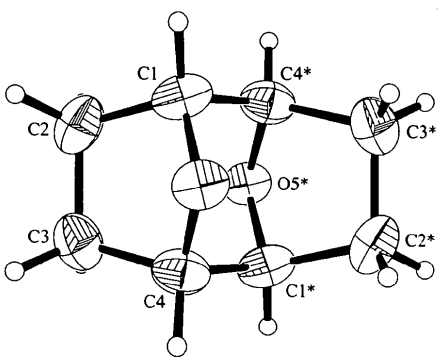


Fig. 3. *XP* (Siemens, 1990) plot of compound (III) with the atomic numbering scheme (50% probability ellipsoids). Atoms marked with an asterisk (*) are in the symmetry position ($-x, 2-y, 1-z$).

Experimental

The crystal of compound (I), prepared according to Haufe (1984), was grown from pure methanol. Compound (II) was synthesized by refluxing cycloocta-1,5-diene with phenylsulfenyl chloride in acetonitrile/water (24:1) for 18 h. The crystal was grown from ethyl ether. Compound (III) was isolated as a 10% by-product in the elimination of the dimesylate of *endo,endo*-2,5-dihydroxy-9-oxabicyclo[4.2.1]nonane by refluxing with potassium carbonate in 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone for 4 h. The crystal was grown from the distilled product mixture.

Compound (I)

Crystal data

$C_8H_{12}Br_2O$
M_r = 284.00
Triclinic
$P\bar{1}$
a = 7.656 (1) Å
b = 7.801 (1) Å
c = 8.547 (1) Å
α = 111.95 (1)°
β = 99.76 (1)°
γ = 90.09 (1)°
V = 465.43 (10) Å^3
Z = 2
D_x = 2.026 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 18.48–21.21°
μ = 8.651 mm^{-1}
T = 293 (2) K
Plate
0.2 × 0.2 × 0.1 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ-scan data (Fair, 1990)
T_{min} = 0.913, T_{max} = 0.999
2034 measured reflections
1890 independent reflections

1277 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 26.26°
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = 0 \rightarrow 10$
3 standard reflections every 250 reflections
intensity decay: 4.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.108

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.636 e Å^{-3}
$\Delta\rho_{min}$ = −0.982 e Å^{-3}

$S = 1.006$
1890 reflections
101 parameters
H atoms calculated and refined riding, with $U_{iso}(H) = 1.2$(or 1.5)U_{eq}(host atom)
$w = 1/[\sigma^2(F_o^2) + (0.068P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.054 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (II)

Crystal data

$C_{20}H_{22}OS_2$
$M_r = 342.50$
Orthorhombic
Pnma
$a = 12.433$ (2) Å
$b = 25.248$ (4) Å
$c = 5.590$ (1) Å
$V = 1754.7$ (5) Å^3
$Z = 4$
$D_x = 1.296$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18.47$–$21.55°$
$\mu = 0.306$ mm^{-1}
$T = 293$ (2) K
Block
0.40 × 0.20 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ-scan data (Fair, 1990)
$T_{min} = 0.909$, $T_{max} = 0.941$
1809 measured reflections
1809 independent reflections
1137 reflections with $I > 2\sigma(I)$
$\theta_{max} = 26.31°$
$h = 0 \rightarrow 15$
$k = -31 \rightarrow 0$
$l = 0 \rightarrow 6$
3 standard reflections every 250 reflections
intensity decay: 1.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.184$
$S = 1.059$
1809 reflections
115 parameters
H atoms calculated and refined riding, with $U_{iso}(H) = 1.2$(or 1.5)U_{eq}(host atom)
$w = 1/[\sigma^2(F_o^2) + (0.1004P)^2 + 0.5007P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.464$ e Å^{-3}
$\Delta\rho_{min} = -0.361$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (III)

Crystal data

$C_8H_{12}O_2$
$M_r = 140.18$
Monoclinic
$P2_1/n$
$a = 6.143$ (1) Å
$b = 6.521$ (1) Å
$c = 9.194$ (1) Å
$\beta = 106.73$ (1)°
$V = 352.71$ (9) Å^3
$Z = 2$
$D_x = 1.320$ Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 41.96$–$44.27°$
$\mu = 0.757$ mm^{-1}
$T = 223$ (2) K
Plate
0.70 × 0.60 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ-scan data (Fair, 1990)
$T_{min} = 0.761$, $T_{max} = 0.860$
756 measured reflections
714 independent reflections
697 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 74.17°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 11$
3 standard reflections every 250 reflections
intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.184$
$S = 1.077$
714 reflections
47 parameters
H atoms calculated and refined riding, with $U_{iso}(H) = 1.2$(or 1.5)U_{eq}(host atom)
$w = 1/[\sigma^2(F_o^2) + (0.0957P)^2 + 0.2883P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.647$ e Å^{-3}
$\Delta\rho_{min} = -0.249$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.105 (15)
Scattering factors from *International Tables for Crystallography* (Vol. C)

The disorder in (II) was handled with the *PART* (*SHELXL*93; Sheldrick, 1993) command. C3*A* and C3*B* were refined using the constraints *EXYZ* and *EADP* (*SHELXL*93); the distances C3*A*—C4*A* and C3*B*—C4*B* were restrained using the *SADI* (*SHELXL*93) command.

For all compounds, data collection: *EXPRESS* (Enraf–Nonius, 1995); cell refinement: *EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93; molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1000). Services for accessing these data are described at the back of the journal.

References

Cope, A. C., McKervey, M. A. & Weinshenker, N. M. (1969). *J. Org. Chem.* **34**, 2229–2231.
Eaton, P. E. & Millikan, R. (1990). *Synthesis*, pp. 483–484.
Enraf–Nonius (1995). *EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Faulkner, D. J. (1996). *Nat. Prod. Rep.* **13**, 75–125, and references therein.
Haufe, G. (1984). *Tetrahedron Lett.* **25**, 4365–4368.
Haufe, G., Alvernhe, G. & Laurent, A. (1990). *J. Fluorine Chem.* **46**, 83–95.
Haufe, G., Kleinpeter, E., Mühlstädt, M. & Graefe, J. (1978). *Monatsh. Chem.* **109**, 575–585.

Kleinpeter, E., Haufe, G., Mühlstädt, M. & Graefe, J. (1977). *Org. Magn. Res.* **9**, 105–107.
Lafont, P. & Vivant, G. (1963). French Patent 1 336 187; (1964). *Chem. Abstr.* **60**, 2803.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1990). *XP. Molecular Graphics Program.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Wahlberg, I. & Eklund, A.-M. (1992). *Prog. Chem. Org. Nat. Prod.* **60**, 1–141.

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Solid Inclusion Compounds of Chiral Roof-Shaped Diamide Hosts

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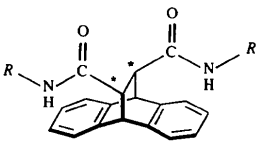
Abstract

The hydrogen-bond-directed inclusion properties of two related enantiomerically pure diamide-type hosts have been investigated. The (11*S*,12*S*)-*trans*-*N*,*N*′-dicyclohexyl-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide host, $C_{30}H_{36}N_2O_2$, (I), formed a quaternary compound when crystallized from a dimethylformamide solution and also includes cyclohexylamine and HCl as guests [(I).DMF.cyclohexylamine.HCl 1:1:1:1], $C_{30}H_{36}N_2O_2.C_6H_{14}N^+.C_3H_7NO.Cl^-$, (I*a*). Three-component crystals were grown from a dimethyl sulphoxide solution of the (11*S*,12*S*)-*trans*-*N*,*N*′-di-*tert*-butyl-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide host, $C_{26}H_{32}N_2O_2$, (II), also containing H_2O as a guest [(II).DMSO.H_2O 1:2:1], $C_{26}H_{32}N_2O_2.2C_2H_6OS.H_2O$, (II*b*). Infinite supramolecular frameworks in both compounds are created involving host and guest molecules in a way that not only host–guest, but guest–guest hydrogen-bonding interactions are observed. However, no direct host–host hydrogen bonds were formed between the chiral diamide molecules (I) or (II).

Comment

Amide molecules usually use their self-complementary hydrogen-bonding functionality to form cyclic dimers or endless chains in crystals (Etter, 1990; MacDonald & Whitesides, 1994). Indeed, hydrogen-bond interactions were observed between closely related racemic diamide hosts (Csöregh, Finge & Weber, 1991) also in the presence of guests with pronounced proton donor and acceptor abilities (*e.g.* methanol and propionic acid).



(I) *R* = cyclohexyl (11*S*,12*S*)
(II) *R* = *tert*-butyl (11*S*,12*S*)
(I*a*) = (I).Cyclohexylamine.DMF.HCl (1:1:1:1)
(II*b*) = (II).DMSO.H_2O (1:2:1)

Contrary to related racemic hosts, the resolved (11*S*,12*S*) chiral diamide hosts (I) and (II) do not form direct host–host hydrogen-bond interactions in the present inclusion compound. Instead, the host functionalities are hydrogen bonded to complementary groups belonging to the guest molecules. Thus, the amide –NH functions of different host molecules in (I*a*) are linked *via* the chloride anion, yielding N(H)···Cl···(H)N interactions, whereas the C=O groups are involved in hydrogen bonding with the cyclohexylamine guest, forming O···(H)N(H)···O connections. The crystal packing is further stabilized by an inter-guest hydrogen bond from the positively charged cyclohexylamine N atom to the Cl^- anion. The infinite supramolecular network thus created (Fig. 3) can be seen to be a result of the tendency to incorporate as many acceptor sites as possible into the hydrogen-bonding scheme (Etter, 1982). The crystalline architecture of (I*a*) is in the form of parallel strings extending along the *a* axis and involving three components of the quaternary compound (Table 1). The fourth component, DMF, though known to be a good proton acceptor (Weber, 1989), is outside the hydrogen-bonding scheme. The proton-acceptor sites are in excess in (I*a*), and in such circumstances the best donor and the best acceptor preferentially form hydrogen bonds to one another (Etter, 1991). Thus, the DMF guest, competing with the host amide C=O groups and the Cl^- ion in (I*a*), is not able to participate in a hydrogen-bonding interaction. The DMF molecules are even found not to be involved in the weak C—H···O interactions and are retained in the voids of the crystal structure only by weak lattice forces, exhibiting rather high mobility [mean U_{iso} of the non-H atoms is 0.22 (2) Å^2]. The hydrogen-bonding pattern in this inclusion compound consists of two 11-membered rings. This corresponds to graph set $R_3^2(11)R_3^2(11)$ (Bernstein *et al.*, 1995).

In (II*b*), on the other hand, each host–NH group is involved in an N(H)···O(=S) interaction with a DMSO guest, known to be an eminent proton accep-

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