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3-Oxa-6,8-diaza-1,2:4,5-dibenzocycloocta-1,4-dien-7-one: a three-dimensional network assembled by hydrogen-bonding, π–π and edge-to-face interactions

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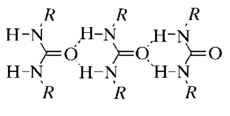
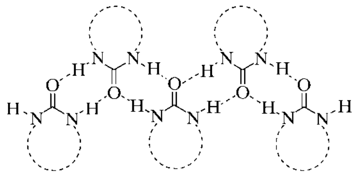
The title compound, $C_{13}H_{10}N_2O_2$, is the first structure in which the urea moiety is incorporated into an eight-membered ring. Two molecules are found in the asymmetric unit, which are almost identical in their conformation and their hydrogen-bond pattern. The carbonyl O atom acts as a double acceptor for the NH groups of two adjacent molecules. In this way, infinite tapes are formed, which are connected *via* π–π and edge-to-face interactions in the second and third dimension. This hierarchical order of interactions is confirmed by molecular mechanics calculations. Force-field and semi-empirical calculations for a single molecule did not find the envelope conformation present in the crystal, indicating instead a C_s conformation. Only with a model consisting of a hydrogen-bonded dimer or a larger hydrogen-bonded section was a conformation found that was similar to the one present in the crystal.

Comment

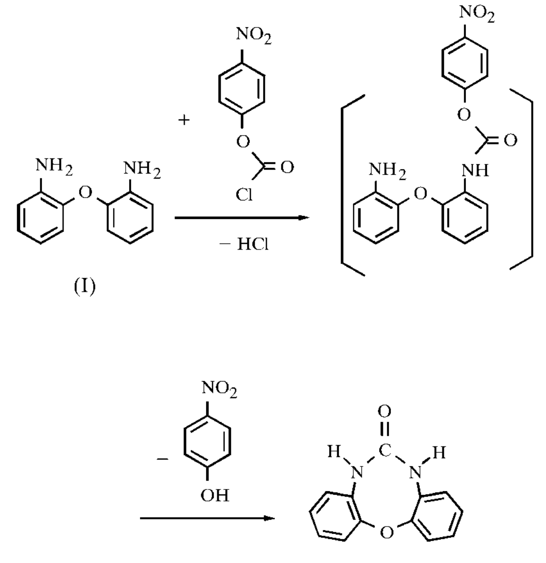
Dialkyl/aryl ureas are self-complementary hydrogen-bond donors and acceptors. They form one-dimensional networks (or chains), (*A*), in which each urea molecule donates two H atoms to the next, thereby chelating the carbonyl O atom. Thus, they are suitable building blocks for supramolecular structures assembled *via* hydrogen bonding (Lortie *et al.*, 2003). Perhaps the most intriguing examples are dimeric capsules (Rebek, 2000; Böhmer & Vysotsky, 2001) formed from calix[4]arenes bearing four urea –NH–C(O)–NH–*R* functions on their wide rim. In cyclic ureas, the amide functions are constrained in a *cis* arrangement so that both the hydrogen-bond donor and acceptor functions point in the same direction. Such cyclic ureas usually adopt tape-like structures, (*B*), in the crystal, provided that no other groups capable of forming hydrogen bonds are present (MacDonald & Whitesides, 1994; Schwiebert *et al.*, 1996; Ebbing *et al.*, 2002).



(*A*)



(*B*)



With the idea of synthesizing new cyclic and linear oligoureas as anion receptors (*e.g.* Scheerder *et al.*, 1994; Boerrigter *et al.*, 1998; Budka *et al.*, 2001; Herges *et al.*, 2002), we undertook the reaction of *o*,*o*-diaminodiphenyl ether, (I), with *p*-nitrophenylchloroformate. From one experiment, the title compound, (II), was obtained as product. This compound was identified as a cyclic urea by its ^1H NMR spectrum. It readily formed single crystals, the structure of which was solved before the mass spectrum confirmed its 'monomeric' nature. The results of the crystal structure determination of (II) are presented here.

Compound (II) is the first example of a crystal structure containing this type of eight-membered heterocycle (Cambridge Structural Database, Version 5.24, March 2003; Allen, 2002). The asymmetric unit contains two almost identical molecules (Fig. 1). A least-squares fit of all non-H atoms yields an r.m.s. deviation of 0.061 Å. The conformation of the eight-membered heterocycle may be described as an envelope consisting of two nearly planar moieties; one contains the C11–C16 aromatic ring (C11*A*–C16*A* for the second molecule in the asymmetric unit) and the attached atoms N1 and O2 (or N1*A* and O2*A*) (r.m.s. deviations 0.012 and 0.021 Å, respectively), while the other contains the C21–C26 aromatic ring (C21*A*–C26*A*) and atoms N2, C1 and O2 (N1*A*, C1*A* and

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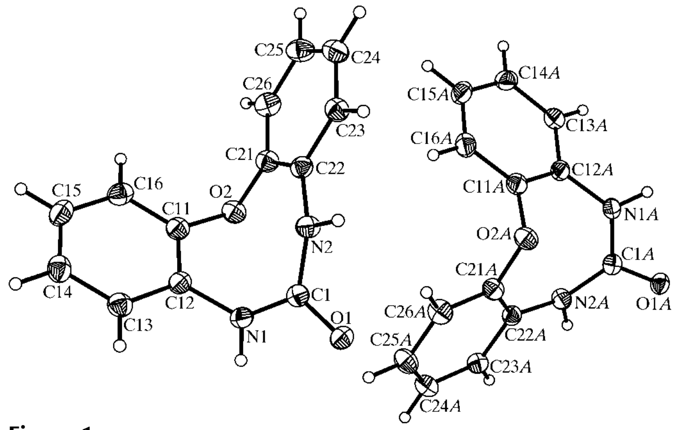

Figure 1

Perspective views of the two independent molecules of (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

O2*A*) (r.m.s. deviations 0.079 and 0.062 Å, respectively). The dihedral angles between these two planes are 72.19 (2) and 68.97 (2)°, respectively. The intra-ring angle at one of the two N atoms (N2 and N2*A*) is considerably widened (Table 1), the other angle (at N1 and N1*A*) only slightly so. The two $\mathrm{N-C_{ar}}$ bonds are of equal length but the $\mathrm{N-C_{carbonyl}}$ bonds differ markedly.

The molecules are arranged *via* hydrogen bonds to form infinite tapes, which include one benzene ring of each molecule. Due to the asymmetric conformation of the cyclic urea, these tapes are not planar and the $D\cdots A$ distances differ. The second benzene ring is oriented perpendicular to the tape, pointing alternately to either side. The distance between parallel rings on one side is 7.00 Å. Their zip-like intercalation leads to the arrangement shown in Fig. 2, where we can distinguish (along the tape) π–π-stacked dimers with centroid separations of 3.91 Å (offset = 1.52 Å and angle = 0°), while the distance between these dimers is 4.07 Å (offset = 2.08 Å and angle = 0°). These values are commensurate with attractive interactions between aromatic rings (Hunter, 1994; Hunter *et al.*, 2001). In addition, as depicted in Fig. 2, the π–π-stacked dimers are held together by two close edge-to-face contacts (centroid separations of 4.80 Å).

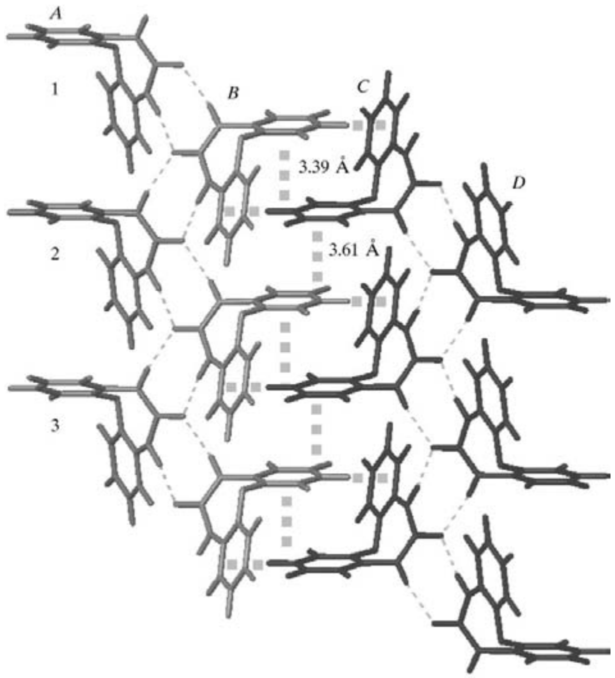

Figure 2

The infinite tapes of hydrogen-bonded molecules of (II) (dashed thin lines), and the connection of these tapes *via* π–π stacking (dashed thick lines) and π–facial hydrogen bonds (squares); the view is along the *a* axis.

The two-dimensional arrangement described so far occurs between symmetry-related molecules of (II). The second molecule in the asymmetric unit displays the same arrangement and both are combined in the third direction, as illustrated in Fig. 3. Here, short contacts of the edge-to-face type (5.15 Å between the centroids of the aromatic rings) are found. These edge-to-face contacts (or π–facial hydrogen bonds) in the crystal are close to the optimum centroid–centroid distance of 5 Å calculated for the 'tilted-T' structure of benzene (Jorgensen & Severance, 1990).

Molecular mechanics calculations with the MM3(96) force field (Allinger *et al.*, 1989; Lii & Allinger, 1989*a*,*b*) showed that

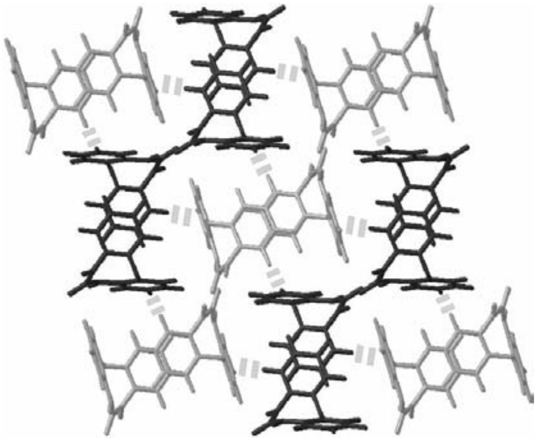

Figure 3

The molecular arrangement of (II) seen along the *c* axis, perpendicular to the π–π stacks. The two molecules in the asymmetric unit are represented as light and dark grey, respectively. Edge-to-face contacts are represented by dashed thick lines.

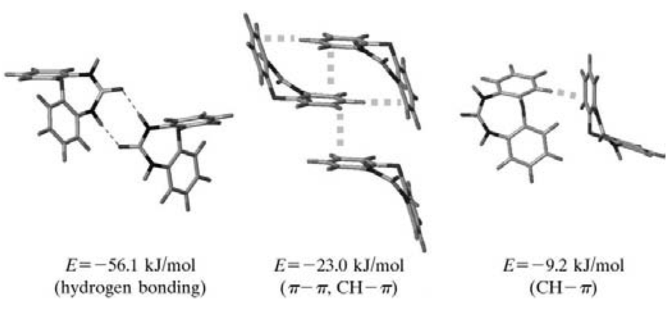

Figure 4

The optimized structures for the central units of the hexameric fragments of the crystal lattice. *E* is the interaction energy per molecule.

the envelope structure found in the crystal does not correspond to the global energy minimum. Instead, the C_s symmetrical conformer (r.m.s. deviation 0.31 Å from the crystal structure) was found to be the lowest in energy; minimization of the crystal structure both with this force field and with the semi-empirical AM1 Hamiltonian (Dewar *et al.*, 1985) in *MOPAC*6 (Stewart, 1990) also ended up in this conformer (Fig. 1). Our attempts to construct a two-dimensional network analogous to Fig. 2 from the C_s symmetrical conformer failed because, in this arrangement, the molecules of (II) cannot simultaneously undergo hydrogen bonding and π–π stacking. To address the question of which molecular interaction induces the conformation in the crystal lattice, we have carried out molecular mechanics calculations on hexameric fragments, as follows: (i) tapes (*A*1–3/*B*1–3 in Fig. 2), (ii) π–π-stacked chains (*B*1–3/*C*1–3), (iii) edge-to-face-bonded oligomers (Fig. 3) and (iv) a hybrid structure of tape and chain (*B*1/2, *C*1/2 and *D*1/2). In these calculations, the corresponding sections of the crystal lattice served as the starting point.

As represented in Fig. 4, the distorted envelope conformations of the π–π-stacked and edge-to-face hexamers converge to the C_s symmetrical structure, while the packing remains similar to that in the crystal [distances between the centroids of the π–π-stacked rings are 3.70 and 4.15 Å, and edge-to-face contacts are 5.00 Å in fragment (ii) and 5.12 Å in fragment (iii)]. In contrast, in the optimized tape structure as well as in the hybrid structure of fragment (iv), all hydrogen-bonded monomers retain their conformation, while in fragment (iv), the π–π-stacked dimers *B*1/2 adopt the C_s symmetrical structure. Although the calculations are for the gas phase rather than for a true crystal lattice, the interaction energies for the central units [*A*2/*B*2 in fragment (i), and *B*2/*C*2 and *C*2/*B*3 in fragment (ii)] allow a rough estimation of the order of magnitude of the non-bonded contacts (*cf.* Fig. 4). The dominating force is hydrogen bonding, followed by π–π stacking and two edge-to-face interactions in the dimers, π–π stacking between the dimers and, weakest, the edge-to-face contacts between the two-dimensional networks.

In summary, the cyclic urea, (II), forms a unique three-dimensional network in the crystal structure, which is built up by hydrogen bonding (calculated interaction energy $E = -56.1$ kJ mol^{-1} per molecule) in one direction, by π–π stacking and edge-to-face interactions ($E = -23.0$ kJ mol^{-1}) in the second dimension and by edge-to-face contacts ($E = -9.2$ kJ mol^{-1}) in the third dimension. Molecular mechanics calculations for hexameric sections of the crystal lattice indicate that the conformation found in the crystal is attributable to hydrogen bonding.

Experimental

Solutions of the bis-trifluoroacetate of bis(2-aminophenyl) ether (150 mg, 0.75 mmol) and of 4-nitrophenyl chloroformate (152 mg, 0.75 mmol) in CH_2Cl_2 (50 ml each) were mixed. A solution of *N*-ethyldiisopropylamine (388 mg, 3 mmol) in CH_2Cl_2 (50 ml) was added dropwise over 2 h. Stirring was continued for the next 4 h. The solvent was removed under reduced pressure and the crude product was triturated with ethyl acetate (30 ml). A white solid was filtered off and identified as the cyclic dimer (25 mg, 15%). The filtrate was washed with 5% sodium carbonate solution and water until the yellow colour of *p*-nitrophenol disappeared. The organic layer was then filtered through silica gel (30 g), which was subsequently washed three times with ethyl acetate (3 × 25 ml). The final product was precipitated from ethyl acetate (5 ml) with hexane (25 ml) as a brown powder (39 mg, 23%). Colourless crystals of (II), suitable for X-ray analysis, separated from a solution of the product in a mixture of tetrahydrofuran and methanol (1:1) upon slow evaporation. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.89 (*s*, NH, 2H), 7.396 (*dd*, Ar-H, 2H, $^3J = 7.8$ Hz, $^4J = 1.0$ Hz) coupled with ^3J to 7.065 (*td*, Ar-H, 2H, $^3J = 7.2$ Hz, $^4J = 1.4$ Hz), 7.028 (*dd*, Ar-H, 2H, $^3J = 8.2$ Hz, $^4J = 2.4$ Hz) coupled with ^3J to 6.98 (*ddd*, Ar-H, 2H, $^3J_1 = 6.8$ Hz, $^3J_2 = 7.8$ Hz, $^4J = 2.4$ Hz); ^{13}C NMR (100 MHz, DMSO-d_6, δ): 154.86, 150.45, 132.89, 126.32, 124.83, 123.30, 123.06; MS (FD) *m*/*z* calculated: 226.24; found: 226.5; m.p. > 489 K (decomposition).

Crystal data

$C_{13}H_{10}N_2O_2$
$M_r = 226.23$
Monoclinic, $P2_1/n$
$a = 17.5679$ (10) Å
$b = 7.1586$ (3) Å
$c = 17.7300$ (10) Å
$\beta = 105.203$ (4)°
$V = 2151.72$ (19) Å^3
$Z = 8$

$D_x = 1.397$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 33 907 reflections
$\theta = 2.2$–27.7°
$\mu = 0.10$ mm^{-1}
$T = 100$ K
Block, colourless
0.42 × 0.32 × 0.28 mm

Data collection

Stoe IPDS-II two-circle diffractometer
ω scans
35 184 measured reflections
5093 independent reflections
4291 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.054$
$\theta_{\rm max} = 27.8°$
$h = -23 \rightarrow 22$
$k = -9 \rightarrow 9$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.093$
$S = 1.05$
5093 reflections
323 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.397P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.24$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.2456 (13)	C1*A*—O1*A*	1.2518 (13)
C1—N1	1.3498 (14)	C1*A*—N1*A*	1.3429 (14)
C1—N2	1.3841 (14)	C1*A*—N2*A*	1.3792 (14)
N1—C12	1.4239 (14)	N1*A*—C12*A*	1.4196 (14)
N2—C22	1.4218 (14)	N2*A*—C22*A*	1.4189 (14)
O2—C21	1.3916 (13)	O2*A*—C21*A*	1.3938 (13)
O2—C11	1.3954 (14)	O2*A*—C11*A*	1.3972 (14)
O1—C1—N1	120.04 (10)	O1*A*—C1*A*—N1*A*	118.90 (10)
O1—C1—N2	117.91 (10)	O1*A*—C1*A*—N2*A*	118.05 (10)
N1—C1—N2	121.90 (10)	N1*A*—C1*A*—N2*A*	122.89 (10)
C1—N1—C12	125.85 (9)	C1*A*—N1*A*—C12*A*	128.26 (9)
C1—N2—C22	135.41 (9)	C1*A*—N2*A*—C22*A*	135.27 (9)
C21—O2—C11	112.03 (8)	C21*A*—O2*A*—C11*A*	112.43 (8)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.877 (16)	2.145 (16)	2.9949 (12)	162.9 (14)
N1*A*—H1*A*···O1*A*^{ii}	0.850 (17)	2.009 (18)	2.8409 (12)	166.0 (15)
N2—H2···O1^{iii}	0.888 (16)	2.075 (16)	2.9564 (12)	172.0 (14)
N2*A*—H2*A*···O1*A*^{iv}	0.899 (17)	2.152 (17)	3.0458 (12)	172.5 (14)

Symmetry codes: (i) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$.

H atoms bonded to C atoms were refined with fixed individual displacement parameters [$U_{\rm iso}$(H) = 1.2 $U_{\rm eq}$(C)], using a riding model with C—H = 0.95 Å. H atoms bonded to N atoms were found in a difference map and refined freely. The conformational search for (II) was performed with the stochastic search routine of the standard MM3(96) force field included in the *SYBYL* program package (TRIPOS Associates Inc., 1996) using the default parameters, except for the number of pushes which was set to 10 000. The conformers obtained from the search were further refined using the full-matrix Newton–Raphson minimization algorithm and characterized as minima or transition states by means of the eigenvalues of the Hessian matrix. Oligomers of (II) were constructed from the crystal structure and submitted to a minimization with the block-diagonal Newton–Raphson method, followed, when possible, by the full-matrix Newton–Raphson algorithm.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1596). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Allinger, N. L., Yuh, Y. H. & Lii, J. H. (1989). *J. Am. Chem. Soc.* **111**, 8551–8566.

Boerrigter, H., Grave, L., Nissink, J. W. M., Chrisstoffels, L. A. J., van der Maas, J. H., Verboom, W., de Jong, F. & Reinhoudt, D. N. (1998). *J. Org. Chem.* **63**, 4174–4180.

Böhmer, V. & Vysotsky, M. O. (2001). *Aust. J. Chem.* **54**, 671–677.

Budka, J., Lhotak, P., Michlova, V. & Stibor, I. (2001). *Tetrahedron Lett.* **42**, 1583–1586.

Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3209–3909.

Ebbing, M. H. K., Vilal, M.-J., Valpuesta, J.-M., Prados, P. & de Mendoza, J. (2002). *Proc. Natl Acad. Sci. USA*, **99**, 4962–4966.

Herges, R., Dikmans, A., Jana, U., Köhler, F., Jones, P. G., Dix, I., Fricke, T. & König, B. (2002). *Eur. J. Org. Chem.* pp. 3004–3014.

Hunter, C. A. (1994). *Chem. Soc. Rev.* **23**, 101–109.

Hunter C. A., Lawson, K. R., Perkins, J. & Urch, C. J. (2001). *J. Chem. Soc. Perkin Trans.* 2, pp. 651–669.

Jorgensen, W. L. & Severance, D. L. J. (1990). *J. Am. Chem. Soc.* **112**, 4768–4774.

Lii, J. H. & Allinger, N. L. (1989*a*). *J. Am. Chem. Soc.* **111**, 8566–8575.

Lii, J. H. & Allinger, N. L. (1989*b*). *J. Am. Chem. Soc.* **111**, 8576–8582.

Lortie, F., Boileau, S. & Boutellier, L. (2003). *Chem. Eur. J.* **9**, 3008–3014.

MacDonald, J. C. & Whitesides, G. M. (1994). *Chem. Rev.* **94**, 2383–2420.

Rebek, J. Jr (2000). *Chem. Commun.* pp. 637–643.

Scheerder, J., Fochi, M., Engbersen, J. F. J. & Reinhoudt, D. N. (1994). *J. Org. Chem.* **59**, 7815–7820.

Schwiebert, K. E., Chin, D. H., MacDonald, J. C. & Whitesides, G. M. (1996). *J. Am. Chem. Soc.* **118**, 4018–4029.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1991). *SHELXTL-Plus.* Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Stewart, J. J. P. (1990). *MOPAC*6.0. QCPE 455. Quantum Chemistry Program Exchange, Indiana University, Bloomingon, Indiana 47405, USA.

Stoe & Cie (2001). *X-AREA*. Stoe & Cie, Darmstadt, Germany.

TRIPOS Associates Inc. (1996). *SYBYL*. Version 6.9. TRIPOS Associates Inc., 1699 S. Hanley Rd, Suite 303, St Louis, Missouri 63144-2913, USA.