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Synthesis of methyl 3,6-dideoxy-3-*C*-methoxycarbonyl-3-*C*-nitrohexopyranosides: crystal structure of methyl 3,6-dideoxy-3-*C*-methoxycarbonyl-3-*C*-nitro-*a*-L-*galacto*-hexopyranoside*

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ABSTRACT

Methyl 3,6-dideoxy-3-*C*-methoxycarbonyl-3-*C*-nitro-*a*-L-*galacto*-hexopyranoside (**3**) has been synthesised by periodate oxidation of methyl *a*-L-rhamnopyranoside followed by condensation with methyl nitroacetate, and its structure has been established on the basis of its analytical and spectral data, and by an X-ray diffraction study. Crystals of **3** are orthorhombic, space group $P2_12_12_1$, with a = 10.009(3), b = 15.3610(3), c = 7.986(3) Å, and Z = 4. Molecular-packing analysis in the atom–atom approach yields an equilibrium configuration in good agreement with the experimental findings.

INTRODUCTION

A large number of antibiotics (rubradirin[1], kijanimicine[2], everninomicine[3], *etc.*) contain 3-*C*-methyl-3-*C*-nitro sugars as structural units. On the other hand, antibiotics of wide clinical use (streptomycin[4] and dihydrostreptomycin[5]) contain 3-branched-chain sugars with an oxygenated functionality (CHO or CH_2OH) at the branch. These facts have aroused interest in the synthesis and properties of sugars having both structural features, *i.e.*, sugars with an oxygenated branch and an NO_2 group at C-3. We now report an application of the Baer reaction[6] (base-catalysed condensation of a glycoside-derived dialdehyde with nitro compounds) for the synthesis of methyl 3,6-dideoxy-3-*C*-methoxycarbonyl-3-*C*-nitrohexopyranosides.

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RESULTS AND DISCUSSION

Treatment of the dialdehyde **1**, obtained by periodate oxidation of methyl α-L-rhamnopyranoside[7], with an ethanolic solution of sodium ethoxide and methyl nitroacetate (**2**) for 5 h at room temperature afforded a mixture of at least three products, from which the main component, methyl 3,6-dideoxy-3-*C*-methoxycarbonyl-

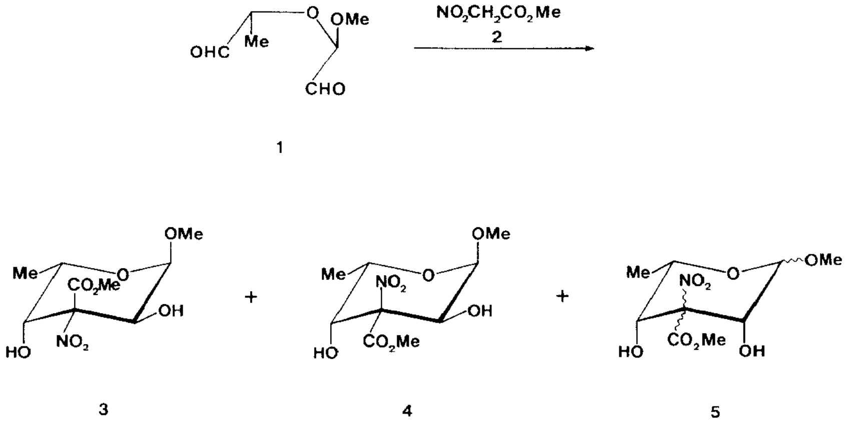


TABLE I

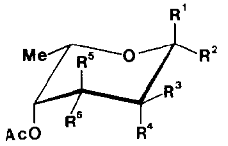
^{1}H-N.m.r. data[a] (δ, p.p.m.) for **3**–**8**

Compound	*H-1*	*H-2*	*H-4*	*H-5*	*OH-2*	*OH-4*	*CO_2Me*	*OMe*	*OAc*	*Me-5*
3	4.82	4.74	4.47	4.41	3.15	2.37	3.87	3.39		1.32
4	4.78	4.60	4.45	4.46	1.80	2.56[b]	3.87	3.37	–	1.30
5	4.87	4.74	4.50	4.28	3.93	3.45	3.77	3.34	–	1.38
6	4.82	5.80	5.82	4.50	–	–	3.80	3.26	2.01 2.09	1.11
7	4.85	5.79	5.81	4.69		–	3.73	3.35	2.13 2.19	1.19
8	4.71	5.84	6.04	4.23	–	–	3.75	3.26	2.02 2.06	1.18

Coupling constants (Hz)

Compound	$J_{1,2}$	$J_{2,4}$	$J_{4,5}$	$J_{5,Me\text{-}5}$	$J_{2,HO\text{-}2}$	$J_{4,HO\text{-}4}$
3	3.5	–	1.2	6.5	10.4	7.0
4	3.3	–	1.3	6.7	10.6	~ 7
5	2.0	1.9	1.6	6.4	5.1	10.9
6	3.4	–	1.5	6.5	–	–
7	3.3	–	1.6	6.6	–	–
8	1.8	1.7	1.6	6.6	–	–

[a] In $CDCl_3$ at 200 MHz. [b] Broad signal.



	R¹	R²	R³	R⁴	R⁵	R⁶
6	OMe	H	OAc	H	CO_2Me	NO_2
7	OMe	H	OAc	H	NO_2	CO_2Me
8	H (or OMe)	OMe (or H)	H	OAc	NO_2 (or CO_2Me)	CO_2Me (or NO_2)

TABLE II

^{13}C-N.m.r. data[a] for **3** and **6**–**8**

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*Me-5*	*OMe*	*$COOCH_3$*	*$COOCH_3$*	*$OCOCH_3$*	*$OCOCH_3$*
3	100.3	67.7	95.3	73.3	66.2	16.3	55.6	53.7	165.9	-	
6	97.2	68.1	91.4	73.1	65.6	16.2	55.6	54.3	164.2	20.1	169.6
										20.5	170.1
7	97.0	67.3	93.1	71.1	63.6	15.8	55.7	54.5	164.0	20.2	169.6
										20.5	169.9
8	98.6	67.0	90.1	69.0	65.3	16.4	55.2	54.3	162.8	20.3	169.9
										20.6	170.0

[a] In acetone-d_6 at 50.3 MHz.

3-*C*-nitro-α-L-*galacto*-hexopyranoside (**3**, >13%), was isolated crystalline. The i.r. spectra of **3** and its diacetate **6** showed absorptions for OH (or OAc), NO_2, and CO_2Me groups. The n.m.r. spectra (Tables I and II) were in accordance with these structures, and the $J_{1,2}$ (~3.4 Hz) and $J_{4,5}$ (~1.3 Hz) values suggested[7,8] H-1,2 and H-4,5 to be *cis*. The strong levorotations of **3** and **6** were in agreement with the α-L configuration. These results, together with the X-ray analysis of **3** (see below), demonstrated the α-L-*galacto* structure.

Column chromatography of the mother liquor of **3** afforded (>7%) a mixture of two isomers (*A* and *B*) of **3**, in the ratio ~2:3 (^{1}H-n.m.r. data). Attempts to isolate *A* and *B* were unsuccessful, but samples enriched either in *A* or in *B* were obtained. The molecular formulae of *A* and *B* were obtained from the analyses of their mixtures, and those of their diacetates. On the basis of the n.m.r. parameters (Tables I and II), the α-L-*gulo* configuration is assigned tentatively to *A* and its diacetate (*i.e.*, **4** and **7**).

The $J_{1,2}$ and $J_{4,5}$ values of **4** and **7** were similar to those of the α-L-*galacto* compounds **3** and **6**, suggesting the same configuration at C-1,2 and C-4,5. This being so, **3** and **4** should be epimeric at C-3. The α-L-*gulo* configuration of **4** was consistent with the fact that C-5 was more shielded in **7** than in **6** ($\Delta\delta$ −2 p.p.m.), which reflected the larger γ-gauche effect anticipated[9] for an axial NO_2 group relative to that of an axial CO_2Me. Likewise, the resonance for H-5 was shifted downfield in **4** and **7**, as would be expected with NO_2 and H-5 in *syn*-diaxial positions because of the larger deshielding effect of NO_2 relative to that of the CO_2Me group.

The long-range coupling ($J_{2,4}$ ~ 1.8 Hz) of *B* and its diacetate indicated H-2 and H-4 to be equatorial, and the $J_{4,5}$ value (1.6 Hz) suggested[7] H-4,5 to be *cis* as shown in **5** and **8**. The $J_{1,2}$ value (1.8–2.0 Hz) did not allow the *cis* ($J_{1,2} \leqslant 1$ Hz)[8a] and the *trans* ($J_{1,2}$ 1.5 Hz)[10] orientation of H-1,2 to be distinguished unambiguously. The configurations at C-1 and C-3 of **5** and **8** remain uncertain.

In spite of the low yield of **3**, the easy access to the crystalline product makes it a suitable candidate for further chemical transformations and biological studies.

X-Ray structure of **3***. — The bond lengths and angles are listed in Table III, and Fig. 1 shows a view of the molecule projected on the (010) plane, with the crystallographic numbering used.

The C–C distances in the pyranose ring are in the range 1.517(7)–1.548(6)Å and in

TABLE III

Bonds lengths (Å) and bond angles (°)[a]

O-1–C-1	1.409(6)	O-81–C-8	1.323(5)
O-1–C-7	1.431(7)	O-82–C-8	1.198(5)
O-2–C-2	1.419(5)	N–C-3	1.527(5)
O-31–N	1.218(5)	C-1–C-2	1.515(7)
O-32–N	1.224(5)	C-2–C-3	1.538(5)
O-4–C-4	1.414(5)	C-3–C-4	1.548(6)
O-5–C-1	1.406(6)	C-3–C-8	1.544(5)
O-5–C-5	1.451(6)	C-4–C-5	1.523(6)
O-81–C-81	1.449(6)	C-5–C-6	1.519(7)
O-1–C-1–C-2	105.2(3)	O-82–C-8–C-3	123.5(4)
O-2–C-2–C-1	110.9(3)	N–C-3–C-2	110.3(3)
O-2–C-2–C-3	115.0(3)	N–C-3–C-8	104.4(3)
O-4–C-2–C-4	108.8(3)	N–C-3–C-4	106.5(3)
O-4–C-4–C-5	109.9(3)	C-1–C-2–C-3	109.0(3)
O-5–C-1–C-2	111.7(4)	C-1–O-5–C-5	113.5(3)
O-5–C-1–O-1	113.8(4)	C-1–O-1–C-7	115.7(4)
O-5–C-5–C-6	106.4(4)	C-2–C-3–C-4	108.2(3)
O-5–C-5–C-4	110.8(3)	C-2–C-3–C-8	115.9(3)
O-31–N–C-3	120.3(4)	C-3–C-4–C-5	109.4(3)
O-32–N–C-3	115.8(4)	C-4–C-3–C-8	111.2(3)
O-38–N–O-31	123.9(4)	C-4–C-5–C-6	112.4(4)
O-81–C-8–O-82	125.9(4)	C-8–O-81–C-81	117.0(4)
O-81–C-8–C-3	110.6(3)		

[a] E.s.d.s. in parentheses.

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* Lists of the observed and calculated structure factors and isotropic thermal parameters are deposited with, and can be obtained from, Elsevier Science Publishers, B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/429/*Carbohydr. Res.*, 199 (1990) 129–137.

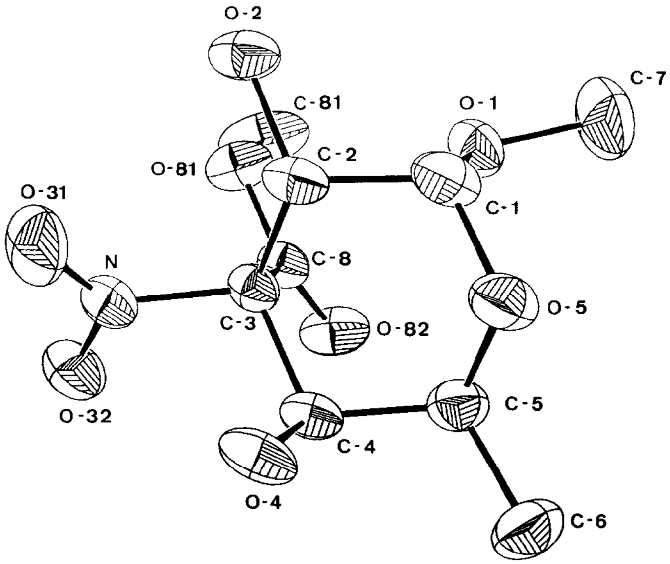

Fig. 1. A perspective view of the molecule of 3 with the numbering scheme.

good agreement with those observed for related structures[11]. The C-1 O-5 bond is significantly shorter than the C-5–O-5 bond, which reflects the anomeric effect[11]. The ring C–O bonds have a mean value of 1.428(6) Å, whereas the exocyclic C-1–O-1 bond is 1.409(6) Å, and the remaining C–OH bonds have a mean value 1.416(5) Å. The interior and exterior ring angles are in the range 104.4(3)–115.9(3)°, consistent with a high degree of tetrahedrality. O-5, C-2, C-3, and C-5 are coplanar (within 0.009 and 0.016 Å), and C-1 and C-4 lie above (0.65 Å) and below (0.70 Å) this plane, respectively. The O-1, C-8, and O-4 substituents are axial, and O-2, N, and C-6 are quasi-equatorial. These results define the *a*-L-*galacto* configuration.

The conformation of the pyranose ring was examined in terms of puckering parameters[12] which, for the atomic sequence O-5, C-1,2,3,4,5, are θ 176°, φ $-10°$, and Q 0.58 Å, and asymmetry parameters[13], which are ΔC_s(O-5) 0.006 and ΔC_2(O-5–C-5) 0.003°, so that the conformation is $^1C_4$.

The crystal contained a three-dimensional network of molecules linked by two intermolecular hydrogen bonds [O-4-H...O-2 $(x+\frac{1}{2}, -y+\frac{1}{2}, -z)$ = 2.762, O-4-H = 0.93, H...O-2 = 1.857Å, O-4-H...O-2 = 164°] and [C-81-H...O-31 $(x, y, z-1)$ = 3.124, C-81-H = 1.08, H...O-4 = 2.539 Å, C-81-H...O-4 = 113°]. There is one intramolecular short contact [O-81...O-2 = 2.769 Å, O-2-H...O-81 = 114°] that could be an intramolecular hydrogen bond.

A minimisation of the crystal lattice energy with respect to lattice constants, molecular translation and rotation, and subrotation of molecular fragments about selected bonds as axes was performed using program PCK6[14a], starting from the experimental structure. The results are given in Table IV, in which changes (%) of lattice

TABLE IV

Molecular-packing analysis.

	A[a]	B[a]	A[b]	B[b]	A[c]	B[c]	A[d]	B[d]	A[e]	B[e]
Cell parameters (%)										
Δa			8.1	3.1	3.3	1.4	3.5	1.2	1.8	1.7
Δb			−2.4	4.1	1.0	0.3	0.8	0.2	0.2	0.5
Δc			1.8	2.9	3.9	2.1	4.2	1.8	2.5	1.2
ΔV			7.5	10.5	8.4	3.9	8.7	3.3	4.5	3.5
Molecular parameters										
Translation (Å)	0.27	0.03	0.39	0.35	0.40	0.14	0.40	0.10	0.07	0.40
Overall molecular rotation (°)	4.5	4.0	6.4	3.0	2.8	1.4	2.0	2.7	2.9	22.7
Sub-rotation ($\Delta\varphi$) (°)										
Δ[O-5–C-1–O-1–C-7]					−19.3	−28.8	−17.1	−17.3	−18.1	−8.5
Δ[C-4–C-3–C-8–O-81]					3.5	9.6	3.8	8.4	3.7	13.9
Δ[C-4–C-3–N–O-32]					−27.2	−9.8	−27.5	−7.2	−11.3	−2.9
Δ[O-5–C-5–C-6–H-6]					−38.7	−17.9				
R[f]	0.044	0.024	0.066	0.049	0.071	0.037	0.070	0.029	0.025	0.146

[a] Cell parameters and torsions fixed at experimental values; *A* excluding and *B* including electrostatic contribution. [b] Optimized cell parameters and torsion fixed. [c] Optimized cell parameters and torsions relaxed. [d] As *c*, but excluding the subrotation around C-5–CH_3. [e] As *d*, but no contribution to the lattice energy of the H-bond. [f] Agreement factor between experimental and theoretical model.

parameters, translations of centre of mass, overall molecular rotation, and changes in relaxed torsion angles are shown. The calculated value of lattice energy (not included) should be higher than the real value because the intramolecular hydrogen bonds were evaluated by van der Waals potential functions and coulombic interactions were ignored. The optimised and experimental structures were similar, the shifts of the positional and orientational molecular parameters were in the ranges 0.03–0.40 Å and 1.4–6.4°, respectively, except for run (*e*) [B] in which the molecular rotation angle was significantly higher (22.7°). The inclusion of the cell parameters as variables leads to a slightly higher expansion in cell volume when the coulombic term is included. The inclusion of molecular flexibility (subrotations) leads to an appreciably lower volume in the runs including electrostatic contribution. The above discrepancies between experimental and theoretical parameters may reflect limitations of the force-field approach, in particular the assumed transferability of potential parameters.

EXPERIMENTAL

General methods. — Melting points were determined with a Büchi apparatus and are uncorrected. Elemental analyses were carried out at the Departamento de Química Analítica, Facultad de Química, Universidad de Sevilla. Optical rotations were measured with a Perkin–Elmer 241 MC polarimeter and i.r. spectra were recorded with a

Perkin–Elmer 299 spectrophotometer. N.m.r. spectra were recorded with a Varian XL-200 spectrometer; ^{13}C resonances were assigned by off-resonance spin-decoupling technique, and ^{1}H resonances by decoupling experiments. Mass spectra were produced with a Kratos MS-80 RFA apparatus. T.l.c. was performed on Kieselgel 60 F_{254} (Merck) with detection by charring with sulphuric acid or u.v. light (254 nm). Silica Gel 60 (Merck) was used for column chromatography. Solutions were concentrated under diminished pressure at 40°.

Reaction of dialdehyde **1** *with methyl nitroacetate* (**2**). — To a solution of **1**[7] (0.8 g, 9.8 mmol) and methyl nitroacetate (1.17 g, 9.8 mmol) in ethanol (10 mL) was added ethanolic M sodium ethoxide (5.2 mL). The solid that precipitated was redissolved by the addition of *N,N*-dimethylformamide. The mixture was stirred for 5 h at room temperature, then neutralised with solid carbon dioxide, and concentrated. A solution of the residue in dichloromethane was filtered and concentrated, and the residue was treated with ether–hexane to give methyl 3,6-dideoxy-3-*C*-methoxycarbonyl-3-*C*-nitro-*α*-L-*galacto*-hexopyranoside (**3**; 0.21 g, 13.5%), m.p. 168–170° (from methanol), $[\alpha]_D^{20}$ $-222°$ (*c* 1, chloroform); ν_{max}^{KBr} 3380 (broad, OH), 1740 (CO_2Me), and 1550 and 1370 cm^{-1} (NO_2). Mass spectrum: *m/z* 266 ($[M+1]^+$, 2%), 235 (100), 234 (73), 188 (18), 176 (10), 160 (33), 143 (59), 127 (67), 110 (80), 99 (24), 87 (9), 83 (10), and 71 (14).

Anal. Calc. for $C_9H_{15}NO_8$: C, 40.76; H, 5.70; N, 5.28. Found: C, 40.49; H, 5.63; N, 5.10.

Column chromatography (hexane–methyl acetate, 1:1) of the material in the mother liquor afforded a mixture (0.10 g, 6.5%) of **4** and **5** in the ratio ~5:8 (^{1}H-n.m.r. data), which could not be resolved; ν_{max} (film) 3470 (broad, OH), 1750 (CO_2Me), and 1560 and 1340 cm^{-1} (NO_2).

Anal. Found: C, 40.48; H, 5.58; N, 5.02.

The n.m.r. data for **3**–**5** are listed in Tables I and II.

*Methyl 2,4-di-O-acetyl-3,6-dideoxy-3-C-methoxycarbonyl-3-C-nitro-α-*L-galacto-*hexopyranoside* (**6**). — Compound **3** (0.17 g) was stirred with acetic acid (0.64 mL), acetic anhydride (0.32 mL), and acetyl chloride (0.40 mL) for 24 h at room temperature. Precipitated **6** (0.22 g, 99%) had m.p. 187–190° (from ether–hexane), $[\alpha]_D^{20}$ $-155°$ (*c* 1, chloroform); ν_{max}^{KBr} 1750 (ester), and 1560 and 1350 (NO_2). Mass spectrum: *m/z* 350 ($[M+1]^+$, 0.5%), 318 (51), 271 (7), 243 (24), 229 (18), 201 (33), 169 (29), 159 (36), 157 (69), 141 (100), 137 (12), 129 (12), 127 (29), and 109 (9).

Anal. Calc. for $C_{13}H_{19}NO_{10}$: C, 44.70; H, 5.48; N, 4.01. Found: C, 44.85; H, 5.67; N, 3.94.

The n.m.r. data for **6** are listed in Tables I and II.

Diacetates **7** *and* **8**. — A mixture of **4** and **5** (0.09 g) was treated conventionally with pyridine (1 mL) and acetic anhydride (1 mL) for 24 h. Preparative t.l.c. (hexane–ethyl acetate, 3:1) of the product gave a mixture (0.11 g, 88%) of **7** and **8** which could not be resolved; ν_{max}^{film} 1755 (ester), 1560 and 1370 cm^{-1} (NO_2).

Anal. Calc. for $C_{13}H_{19}NO_{10}$: C, 44.70; H, 5.48; N, 4.01. Found: C, 44.49; H, 5.44; N, 3.77.

The n.m.r. data for **7** and **8** are listed in Tables I and II.

Crystal data for **3**. — Crystals of $C_9H_{12}NO_8$ (M_r 265.2) were orthorhombic, space group $P2_12_12_1$, with a = 10.009(2), b = 15.3610(3), c = 7.986(6) Å, V = 1227.8(6) Å^3, Z = 4, $D_c = D_m$ = 1.43 g.cm^{-3}, μ(Mo − K_α) = 0.12 mm^{-1}, and F(000) = 560. Unit-cell parameters were obtained from the least-squares refinement of values of 25 reflections ($4 < \theta < 14$), using an Enraf-Nonius CAD-4 diffractometer. Mo-K_α radiation, λ = 0.71069 Å (graphite monochromator). A total of 2018 reflections were scanned ($0 \leqslant h \leqslant 14, 0 \leqslant k \leqslant 21, 0 \leqslant l \leqslant 11$) and measured in the $2\theta < 60°$ range, $\omega - 2\theta$ mode. Two standard reflections ($1\bar{3}\bar{2}$ and 132), monitored every 100 reflections, showed statistical fluctuations; 1753 observed reflections [$I \leqslant 2\sigma(I_0)$] were used for the structure determination. Corrections were made for Lorentz and polarisation factors; absorption and extinction were ignored. The structure was solved by direct methods using the MULTAN-80 programme[15]. 222 E values ($E > 1.51$) were used as input to Multan, and the correct set, with the highest figure of merit of 3.00 and a residual value of 19.48, gave approximate positions for 11 of the 18 non-H atoms; the remaining atoms were located from a Fourier synthesis. F was refined by full-matrix least squares. A difference Fourier synthesis up to sin θ/λ = 0.45 Å^{-1} revealed the H atoms. Further refinement of F with non-H atoms isotropically produced convergence with R = 0.004, R_w = 0.04 [$w^{-1} = \sigma^2(F)$], and S = 0.87. The thermal parameters assigned to H atoms were equal to those of bonded atoms. A final difference Fourier synthesis showed $\Delta\rho = \pm 0.3$ e Å^{-3}. Maximum least-squares shift to error was 0.02. The XRAY-70 system[16] of computer programs was used. Atomic scattering factors were obtained from International Tables for X-Ray Crystallography[17].

Potential functions in the form $\varphi = -\mathrm{A}\, r^{-6} + \mathrm{B} \exp(cr) + Kqq'/r$ were used to represent the non-bonded interaction potential energy. The set of potential parameters included coefficients fitted by Williams[14b] for C···C and H···H interactions, by Govers[18] for N···N, and the parameters of Mason and Kreevoy[19] for O···O. For mixed interactions, the combination rules of Mirskaya[20] were used. Several runs of the energy minimisation were carried out for both, excluding and including electrostatic contribution, [exp (-6)] and [exp (-6-1)], respectively. For the calculations including the electrostatic contribution to the non-bonded interactions, the partial effective charge at an atom was estimated from the percentage of covalent character of bonds involving that atom[21].

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