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Directly Linked *C*-Disaccharides: Structures of Two 3,4-Dihydro-2*H*-pyran Derivatives

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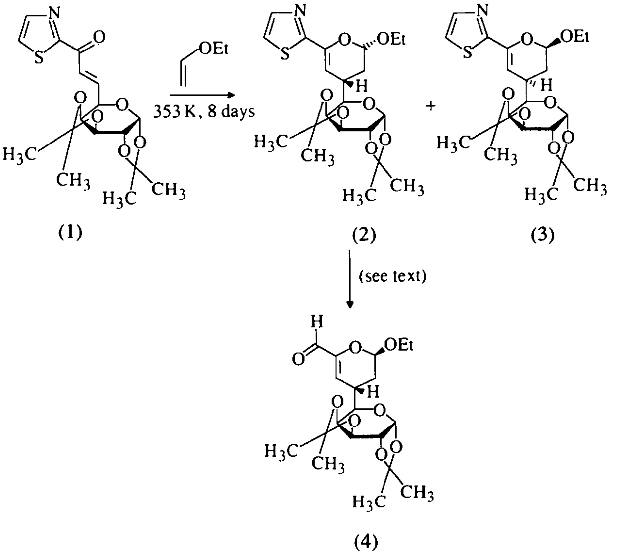
Abstract

Analysis of the crystal structures of the two diastereomeric *C*-disaccharides, (2*R*,4*R*)-4-(1,2;3,4-di-*O*-isopropylidene-α-D-*galacto*-1,5-pyranose-5-yl)-2-ethoxy-6-(2-thiazolyl)-3,4-dihydro-2*H*-pyran, $C_{21}H_{29}NO_7S$, (3), and (2*R*,4*S*)-4-(1,2;3,4-di-*O*-isopropylidene-α-D-*galacto*-1,5-pyranose-5-yl)-2-ethoxy-6-formyl-3,4-dihydro-2*H*-pyran, $C_{19}H_{28}O_8$, (4), allows the definition of the absolute configurations of the products of the cycloaddition reaction between 1-oxa-1,3-butadiene and ethyl vinyl ether. The relevant conformational aspects of the two molecules are discussed. In the crystals of (3), a water molecule participates in hydrogen bonds to the thiazole N atom and an O atom of a dioxapentane ring of the sugar moiety within the same molecule.

Comment

Recent work by Dondoni and co-workers has been directed towards the synthesis of *C*-disaccharides wherein the two sugars are directly linked by a C—C bond (Dondoni, Kniezo & Martinkova, 1994, 1996). The interest in this hitherto scarcely explored class of sugar analogues (Danishefsky & Barbachyn, 1985; Lopez & Fraser-Reid, 1989; Armstrong & Teegarden, 1992) stems from their properties as re-engineered disaccharides with predictable restricted conformations, and as their potential use as glycosidase inhibitors. The synthetic method employed by Dondoni and co-workers involves the *de novo* construction of a second pyranose ring on an existing one by an asymmetric hetero-Diels–Alder (HDA) reaction (Boger & Weinreb, 1987; Waldmann, 1994). Thus, the cycloaddition reaction between the galactosyl-bearing 1-oxa-1,3-butadiene, (1), and ethyl vinyl ether led to a mixture of diastereomeric 3,4-dihydro-2*H*-pyran derivatives (2) and (3) in 4:1 ratio and 97% total yield. Suitable synthetic elaborations of the newly formed 3,4-dihydropyran ring of these compounds (*i.e.* conversion of the thiazole ring into the formyl group and hydroxylation of the double bond) afforded the target diastereomeric *C*-disaccharides.



The relative configuration at the newly formed stereocentres of (2) and (3) was obtained by analysis of the ^{1}H NMR spectra. The X-ray crystal structure determination of (3) and (4) defined their absolute stereochemistry while that of the major diastereomer (2), which did not give crystals suitable for an X-ray analysis, was deduced from that of (4) which was derived from (2) by thiazolyl-to-formyl conversion and epimerization at C2 of the dihydropyran ring.

As shown in the scheme and the figures, the configurations at C6 are opposite in (3) and (4) being *R* and *S*, respectively, while at the other chiral centres, the configurations are identical for the two compounds: *R* at C7, C11, C13 and *S* at C8, C10 of the *galacto*-pyranosyl

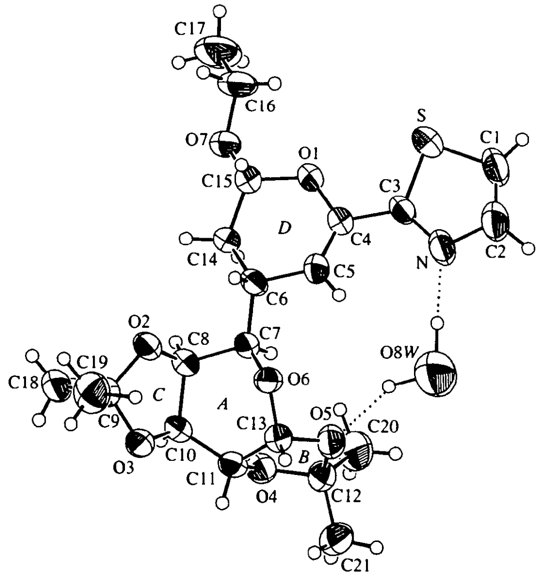


Fig. 1. *ORTEP* (Johnson, 1965) drawing of (3). Displacement ellipsoids are drawn at the 50% probability level.

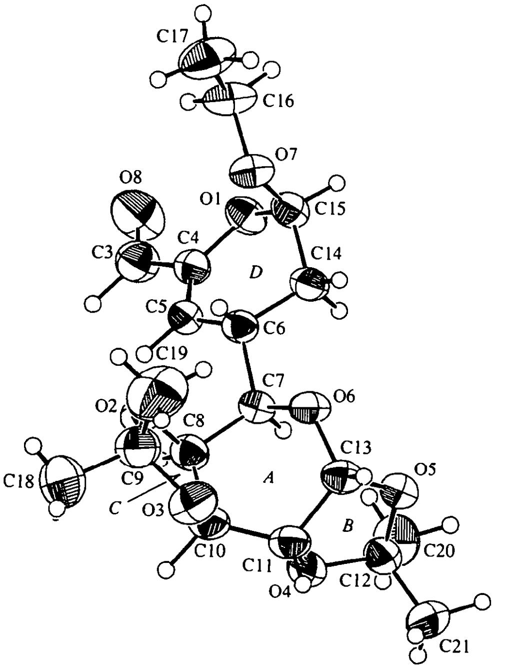


Fig. 2. *ORTEP* (Johnson, 1965) drawing of (4). Displacement ellipsoids are drawn at the 50% probability level.

moiety and also *R* at C15, according to the chirality of the common precursor D-galactose used in the syntheses.

The thiazolyl and formyl substituents in (3) and (4), respectively, tend to be coplanar with the C4(O1)C5 system indicating some π-conjugation through C3—C4. The twist from coplanarity is larger for the first compound, as indicated by the values of the S—C3—C4—C5 and O8—C3—C4—C5 torsion angles quoted in Tables 2 and 4. In both cases, the substituents are oriented such that S or O8 lies on the same side of the C3—C4 bond as O1 (*Z* configuration) and therefore *trans* to the C4═C5 double bond, with the vicinal 1,4 intramolecular contacts [S···O1 = 2.854 (2) and O8···O1 = 2.699 (3) Å] being shorter than the sum of van der Waals radii (S···O = 3.24, O···O = 3.00 Å; Bondi, 1964). While it has been known for a long time that sulfur can approach other atoms at 'non-bonded' distances much shorter than the sum of the van der Waals radii (Donohue, 1950; Nardelli, Braibanti & Fava, 1957; Lozac'h, 1971; Abrahamsson, Rehenberg, Liljefors & Sandstrom, 1974; Abrahamsson & Zacharis, 1976), the same cannot be said about the O···O contacts, but a search in the Cambridge Structural Database (Allen *et al.*, 1991) shows that the contact present in (4) falls in the most populated range of values (2.68–2.72 Å) for this kind of non-bonded contact.

As expected, the thiazoline ring is planar, with bond distances and angles agreeing quite well with those found in the two compounds of this series studied previously (Dondoni, Ianelli, Kniezo, Merino & Nardelli, 1994). The total puckering amplitude (Cremer & Pople, 1975) of the O1-dihydropyran ring *D* [Q_T = 0.477 (4) in (3), 0.471 (3) Å in (4)] is reduced with respect to that of the O6-pyranose ring *A* [Q_T = 0.602 (3) in (3), 0.629 (2) Å in (4)] as a consequence of the presence of the double bond. Both rings have a half-chair conformation with a local pseudo twofold axis running through the mid-points of the C4—C5 and C14—C15 bonds in the former, and the mid-points of the O6—C7 and C10—C11 bonds in the latter.

The conformations of the dioxapentane rings of the sugar moiety (rings *B* and *C*) lie between envelope and half-chair and their puckering amplitudes [ring *B*: Q_T = 0.310 (3) in (3), 0.310 (3) Å in (4); ring *C*: Q_T = 0.314 (3) in (3), 0.246 (2) Å in (4)] are not significantly different in the two compounds, with the exception of ring *C* of (4) which is less puckered, and this is related to the fact that the O2—C8 and O2—C9 bonds are shorter and the angle C8—O2—C9 larger in (4) (Tables 2 and 4), but it is doubtful that these findings correspond to a real structural situation.

The ethoxy group is oriented in the same way in both compounds, *i.e.* with the O7—C16 bond antiperiplanar to the C14—C15 bond (Tables 2 and 4). The difference of chirality at C6 justifies the difference of the torsion angles about the C6—C7 bond in the two compounds. In particular, C6—C14 is (−)antiperiplanar to C7—O6 and (−)synclinal to C7—C8 in (3), while it is (+)-antiperiplanar to C7—C8 and (+)synclinal to C7—O6 in (4) (Tables 2 and 4).

The overall conformation of the core of the two molecules is similar, as indicated by the following values of the dihedral angles formed by the normals to the weighted least-squares planes through the rings: A/B = 73.2 (1), A/C = 78.0 (1), A/D = 36.4 (1)° for (3), and A/B = 77.7 (1), A/C = 85.9 (1), A/D = 27.9 (1)° for (4).

In the crystal structure of (3), the molecular conformation and packing conditions are such as to leave a hole in which a water molecule is settled forming two hydrogen bonds with the thiazole N atom [O8W—H2OW = 0.98, O8$W\cdots$N = 2.964 (4), H2O$W\cdots$N = 1.98 Å, O8W—H2O$W\cdots$N = 177°] and an O atom of one dioxapentane ring of the sugar moiety [O8W—H1OW = 0.95, O8$W\cdots$O5 = 2.988 (4), H1O$W\cdots$O5 = 2.10 Å, O8W—H1O$W\cdots$O5 = 155°] (Fig. 1). It is possible that this hydrogen bonding cooperates in inducing the observed conformation.

Experimental

The preparation of the compounds will be published elsewhere (Dondoni, Kniezo & Martinkova, 1996).

Compound (3)

Crystal data

$C_{21}H_{29}NO_7S.H_2O$
M_r = 457.54
Orthorhombic
$P2_12_12_1$
a = 23.826 (7) Å
b = 10.098 (4) Å
c = 9.881 (4) Å
V = 2377 (2) Å^3
Z = 4
D_x = 1.278 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 30 reflections
θ = 25–39°
μ = 1.596 mm^{-1}
T = 293 (2) K
Small prism
0.38 × 0.29 × 0.21 mm
Colourless

Data collection

Siemens AED diffractometer
θ–2θ scans
Absorption correction: none
2597 measured reflections
2580 independent reflections
1559 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.0265

$\theta_{\rm max}$ = 70.1°
$h = -28 \rightarrow 28$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 12$
1 standard reflection monitored every 50 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.0313
$wR(F^2)$ = 0.0497
S = 0.904
2577 reflections
387 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0206P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.026$

$\Delta\rho_{\rm max}$ = 0.13 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.13 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.04 (3)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (3)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S	−0.01574 (3)	−0.00531 (11)	−0.40832 (12)	0.0781 (4)
N	0.04690 (11)	0.1881 (3)	−0.3415 (3)	0.0791 (10)
O1	0.09003 (8)	−0.1315 (2)	−0.4499 (3)	0.0627 (7)
O2	0.32033 (8)	−0.1189 (2)	−0.3632 (2)	0.0587 (7)
O3	0.39054 (8)	0.0301 (2)	−0.3722 (3)	0.0612 (7)
O4	0.31699 (8)	0.2767 (2)	−0.5613 (2)	0.0538 (6)
O5	0.25424 (8)	0.3340 (2)	−0.4000 (2)	0.0622 (7)
O6	0.26026 (8)	0.1265 (2)	−0.3020 (2)	0.0472 (6)
O7	0.12493 (8)	−0.3161 (2)	−0.5518 (3)	0.0690 (8)
C1	−0.0463 (2)	0.1418 (4)	−0.3724 (5)	0.0778 (13)
C2	−0.0086 (2)	0.2299 (5)	−0.3415 (5)	0.091 (2)
C3	0.04876 (12)	0.0644 (3)	−0.3733 (4)	0.0517 (9)
C4	0.10012 (12)	−0.0159 (3)	−0.3843 (4)	0.0492 (8)
C5	0.15024 (14)	0.0217 (3)	−0.3394 (3)	0.0490 (9)
C6	0.20274 (12)	−0.0530 (3)	−0.3682 (4)	0.0474 (9)
C7	0.24851 (12)	0.0412 (3)	−0.4145 (4)	0.0434 (8)
C8	0.30219 (12)	−0.0241 (3)	−0.4628 (4)	0.0498 (9)
C9	0.38003 (13)	−0.1063 (3)	−0.3497 (4)	0.0559 (10)
C10	0.35171 (13)	0.0742 (3)	−0.4712 (4)	0.0478 (9)
C11	0.33763 (13)	0.2175 (3)	−0.4412 (4)	0.0499 (9)
C12	0.28049 (14)	0.3834 (4)	−0.5217 (4)	0.0574 (10)
C13	0.29074 (13)	0.2404 (3)	−0.3370 (4)	0.0504 (9)
C14	0.19043 (14)	−0.1593 (4)	−0.4752 (5)	0.0542 (10)
C15	0.13540 (13)	−0.2273 (4)	−0.4481 (5)	0.0559 (10)
C16	0.0758 (2)	−0.3980 (5)	−0.5283 (6)	0.095 (2)
C17	0.0648 (2)	−0.4742 (5)	−0.6526 (6)	0.140 (2)
C18	0.4084 (2)	−0.1906 (5)	−0.4547 (7)	0.0781 (15)
C19	0.3950 (2)	−0.1389 (6)	−0.2051 (6)	0.0880 (15)
C20	0.2370 (2)	0.4027 (5)	−0.6297 (6)	0.0837 (15)
C21	0.3130 (2)	0.5073 (5)	−0.4897 (6)	0.0725 (12)
O8W	0.13791 (12)	0.3838 (3)	−0.2991 (3)	0.1346 (13)

Table 2. *Selected geometric parameters (Å, °) for (3)*

S—C1	1.692 (5)	O1—C4	1.357 (4)
S—C3	1.725 (3)	C1—C2	1.302 (6)
N—C2	1.388 (5)	C3—C4	1.472 (4)
N—C3	1.289 (5)	C4—C5	1.329 (5)
C1—S—C3	89.1 (2)	S—C3—C4	120.1 (2)
C2—N—C3	109.1 (3)	O1—C4—C3	111.2 (3)
S—C1—C2	110.6 (4)	C3—C4—C5	124.4 (3)
N—C2—C1	116.8 (4)	O1—C4—C5	124.3 (3)
S—C3—N	114.4 (3)	C4—C5—C6	123.2 (3)
N—C3—C4	125.5 (3)		
S—C3—C4—C5	−168.8 (3)	C14—C6—C7—C8	−52.0 (4)
C14—C6—C7—O6	−174.2 (3)	C6—C7—C8—O2	−50.1 (4)

Compound (4)

Crystal data

$C_{19}H_{28}O_8$
M_r = 384.42
Orthorhombic
$P2_12_12_1$
a = 17.339 (4) Å
b = 16.430 (5) Å
c = 7.222 (3) Å
V = 2057.4 (12) Å^3
Z = 4
D_x = 1.241 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 29 reflections
θ = 18–35°
μ = 0.808 mm^{-1}
T = 293 (2) K
Small prism
0.42 × 0.23 × 0.19 mm
Colourless

Data collection

Siemens AED diffractometer
θ–2θ scans
Absorption correction: none

$\theta_{\rm max}$ = 70.4°
$h = -21 \rightarrow 21$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 8$

7810 measured reflections
3918 independent reflections
1864 observed reflections
$[I > 2\sigma(I)]$
$R_{int} = 0.0418$

1 standard reflection
monitored every 50
reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0284$
$wR(F^2) = 0.0409$
$S = 0.797$
3916 reflections
347 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0138P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.097$
$\Delta\rho_{max} = 0.09$ e Å^{-3}
$\Delta\rho_{min} = -0.10$ e Å^{-3}

Extinction correction:
*SHELXL*93 (Sheldrick, 1993)
Extinction coefficient:
0.00217 (7)
Atomic scattering factors
from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration:
Flack (1983)
Flack parameter =
−0.21 (17)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (4)*

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

	x	y	z	U_{eq}
O1	1.04398 (8)	0.13883 (9)	1.2628 (2)	0.0536 (10)
O2	0.73061 (10)	0.12088 (11)	1.2065 (3)	0.0773 (12)
O3	0.64200 (9)	0.15231 (11)	0.9890 (3)	0.0734 (11)
O4	0.73737 (9)	0.33962 (10)	0.8670 (2)	0.0592 (11)
O5	0.81216 (10)	0.27669 (11)	0.6544 (2)	0.0602 (11)
O6	0.81046 (9)	0.16283 (9)	0.8470 (2)	0.0509 (10)
O7	1.00207 (9)	0.01552 (10)	1.1391 (2)	0.0550 (10)
O8	1.06433 (12)	0.19071 (13)	1.6140 (3)	0.0937 (14)
C3	1.0004 (2)	0.1920 (2)	1.5476 (4)	0.067 (2)
C4	0.98142 (14)	0.16419 (15)	1.3603 (4)	0.047 (2)
C5	0.90964 (15)	0.1645 (2)	1.3021 (4)	0.0474 (15)
C6	0.88716 (13)	0.1386 (2)	1.1116 (4)	0.0450 (13)
C7	0.82633 (14)	0.19437 (14)	1.0282 (4)	0.044 (2)
C8	0.75165 (15)	0.1991 (2)	1.1397 (4)	0.052 (2)
C9	0.6590 (2)	0.0962 (2)	1.1339 (5)	0.071 (2)
C10	0.68253 (15)	0.2270 (2)	1.0255 (4)	0.056 (2)
C11	0.70286 (15)	0.26129 (15)	0.8378 (4)	0.055 (2)
C12	0.78508 (14)	0.3549 (2)	0.7114 (4)	0.060 (2)
C13	0.76527 (14)	0.2145 (2)	0.7347 (4)	0.053 (2)
C14	0.9602 (2)	0.1355 (2)	0.9941 (4)	0.052 (2)
C15	1.0250 (2)	0.0951 (2)	1.0962 (4)	0.052 (2)
C16	1.0593 (2)	−0.0300 (2)	1.2379 (6)	0.074 (2)
C17	1.0354 (3)	−0.1177 (2)	1.2319 (7)	0.093 (4)
C18	0.5976 (3)	0.1003 (3)	1.2810 (8)	0.103 (3)
C19	0.6666 (2)	0.0126 (2)	1.0457 (5)	0.119 (4)
C20	0.8534 (2)	0.4058 (3)	0.7718 (7)	0.081 (3)
C21	0.7395 (2)	0.3928 (3)	0.5546 (6)	0.078 (2)

Table 4. *Selected geometric parameters (Å, °) for (4)*

O8—C3	1.209 (4)	C3—C4	1.465 (4)
O8—C3—C4	124.5 (3)		
C7—O6—C13—O5	80.5 (2)	C14—C6—C7—O6	58.6 (3)
C16—O7—C15—C14	−179.9 (2)	C14—C6—C7—C8	179.5 (2)
O8—C3—C4—C5	177.0 (3)	C6—C7—C8—O2	−40.9 (3)

All H atoms were refined isotropically as free atoms, excepting those of the C17 methyl groups of (3) and C19 of (4), which show rather high thermal motion (or disorder). These methyl H atoms were refined using the HFIX 137 option in *SHELXL*93 (Sheldrick, 1993) which calculates a difference electron-density synthesis around the circle which represents the loci of possible H-atom positions for a fixed C—H distance and C—C—H angle. Also, the water molecule in (3) is affected by high thermal motion (or disorder) as indicated by the value of U_{eq} of its O atom; its two H atoms were located from a $\Delta\rho$ synthesis and not refined.

The absolute configurations were assigned on the basis of refined Flack (Flack, 1983) index giving, for both molecules, configurations in agreement with the known chirality of galactose used in the syntheses.

For both compounds, data collection: local programs (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979); cell refinement: *LQPARM* (Nardelli & Mangia, 1984); data reduction: local programs; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *PARST* (Nardelli, 1983, 1995); *PARSTCIF* (Nardelli, 1991).

The authors are grateful to Professor Alessandro Dondoni (University of Ferrara) who kindly supplied crystals of the compounds.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$C_{38}H_{54}N_3O_9P$, a New Compound in Diazadihydrophosphinine Chemistry

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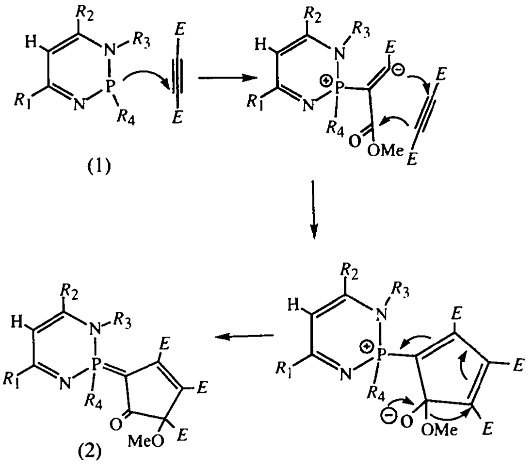
Abstract

Another compound of the diazadihydrophosphinine family has been isolated and structurally characterized. This new compound in diazadihydrophosphinine chemistry was identified as trimethyl 5-[4-*tert*-butyl-1-cyclohexyl-2-diisopropylamino-6-(4-methoxyphenyl)-1,2-dihydro-1,3,2-diazaphosphin-2-ylidene]-3-methoxy-4-oxo-1-cyclopentene-1,2,3-tricarboxylate, $C_{38}H_{54}N_3O_9P$. The parent dihydrodiazaphosphin structure is still present in the new compound and the P atom is linked by a double bond to a five-membered ring. The P(1)—C(31) bond distance is 1.731 (8) Å. The five-membered ring is planar [maximum deviation from the least-squares plane of 0.011 (9) Å for C(35)] and the ylidic charge at Cα to the P atom is stabilized by the electron-attracting groups in the ring.

Comment

Recently we reported on the reactivity of diazadihydrophosphinines, (1), towards one equivalent of dimethylacetylenedicarboxilate (DMAD) (Barluenga, Tomás, Bieger, García-Granda & Santiago-García, 1996). The reaction afforded a bicyclo[3,2,1]phospha-2,8-diaza-1,3,6-octatriene that showed an unexpected reactivity towards electrophiles, leading to polycyclic products in high yields. As DMAD can also be seen as an electrophile, we made a one-pot attempt to gain insight into its reactivity. At high concentrations of DMAD, the major product, (2), was afforded according to ^{31}P-NMR; this was isolated by chromatography and finally obtained in the form of yellow crystals. It was characterized by spectroscopic methods but the structure could not be established without ambiguities. Single crystals were grown from ether/hexane and a diffraction study was performed on one of them. It showed that in the final product, the parent dihydrodiazaphosphin structure was still present. The P atom was linked by a P═C double bond to a five-membered ring system resulting from the interaction with two molecules of DMAD. The mechanism of the reaction is shown in the scheme below.



$R_1 = {}^t$Bu $\quad R_3 =$ cHex $\quad E = CO_2Me$
$R_2 =$ 4-$C_6H_4OCH_3$ $\quad R_4 = N^iPr_2$

The compound was identified as 4-^{t}butyl-1-cyclohexyl-2-diisopropylamino-6-(4-methoxyphenyl)-2-[4-methoxy-2,3,4-tris(methoxycarbonyl)-5-oxo-2-cyclopentenyliden]-1,2-dihydro-1,3,2-diazaphosphinine, (2). The structure resembles a molecule obtained by Tebby and co-workers (Waite, Tebby, Ward & Williams, 1969) by the reaction of DMAD with triphenylphosphine, but in that case no structural data were reported. In the structure itself, most bond parameters are in the expected ranges but the P—N single bonds are shortened, probably as the result of to p–σ^* interactions (Gilheany, 1994). These interactions should also be responsible for the flattening of the N atoms indicated by the sums of the corresponding bond angles [359.2 (18) and 357.8 (16)°, respectively, in the two tricoordinated cases].

The six-membered ring [P(1),N(2),C(3),C(4),C(5),-N(6)] has a skew-boat conformation approaching the $^1S_2$ form in the notation of Boeyens (1978). The Cremer & Pople (1975) ring-puckering parameters are q_2 = 0.445 (7), q_3 = 0.165 (7), Q = 0.474 (6) Å, φ = 22 (1), θ = 70 (1)°. In the six-membered ring, mesomeric stabilization can be observed; this provokes a slight shortening of the single and a widening of the double bonds.

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