Glycosyl cations in glycosylation reactions

Hansen, T.

Glycosyl Cations in Glycosylation Reactions

PROEFSCHRIFT

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de graad van Doctor aan de Universiteit Leiden,
op gezag van Rector Magnificus prof. mr. C. J. J. M. Stolker,
volgens besluit van het College voor Promoties
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door

Thomas Hansen

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The cover depicts the conformational energy landscape of the elusive glycosyl cation, which is one of the key reactive intermediates in glycosylation reactions.

Adapted from Hansen *et al.*, *ACS Cent. Sci.* **2019**, 5 (5).

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Ac	acetyl
AIBN	2,2'-azobis(2-methyl-propionitrile)
All	allyl
APT	attached proton test
aq.	aqueous
Ar	aryl
Ara	arabinose
Arom	aromatic
ASM	activation strain model
B	boat
B3LYP	Becke, 3-parameter, Lee-Yang-Parr
BAIB	(diacetoxyiodo)benzene
Bn	benzyl
bs	broad singlet
BSP	1-benzenesulfinylpiperidine
Bu	butyl
Bz	benzoyl
C	chair
cal	calorie
calcd	calculated
Car	caryophyllose
cat.	catalytic
CBz	carboxybenzyl
CDI	carbonyldiimidazole
CEL	conformational energy landscape
CID	collision induced dissociation
CIP	contact ion pair
COSY	correlation spectroscopy
C_q	quaternary carbon atom
CSA	camphor-10-sulfonic acid
Cy	cyclohexyl
δ	chemical shift
d	doublet
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCE	1,2-dichloroethane
DCM	dichloromethane
dd	double doublet
ddd	doublet of double doublets
dddd	double doublet of double doublets
ddt	doublet of double triplets
DEAD	diethyl azocarboxylate
DFE	difluoroethanol
DFT	density function theory
DiPEA	diisopropylethylamine
DMAP	4-dimethylaminopyridine
DMF	dimethylformamide
DMNPA	2,2-dimethyl-2-(*ortho*-nitrophenyl)
DMP	Dess-Martin periodinane
DMSO	dimethylsulfoxide
DPS	diphenylsulfoxide
dq	double quartet
dt	double triplet
dtd	doublet of triple doublets
DTBMP	2,6-di-*tert*-butyl-4-methylpyridine
DTBS	di-*tert*-butylsilylidene
E	energy
E	envelope
EDA	energy decomposition analysis
eq.	molar equivalent
Et	ethyl
E-X	electrophilic activator system
Fuc	fucose
FT	Fourier transform
gg	*gauche-gauche*
gt	*gauche-trans*
GATED	proton decoupling applied only during relaxation
Gal	galactose
Glc	glucose
GlcA	glucuronic acid
$GlcN_3$	2-azido-2-deoxy glucose
h	hour(s)
H	half-chair
HATU	1-[bis(dimethylamino)methylene]-1*H*-1,2,3-triazolo[4,5-*b*]pyridinium 3-oxide hexafluorophosphate
HFIP	hexafluoro-*iso*-propanol
HMBC	heteronuclear multiple-bond correlation spectroscopy
HOMO	highest occupied molecular orbital
HPLC	high performance liquid chromatography
HRMS	high-resolution mass spectroscopy
HSQC	heteronuclear single quantum coherence
IDCP	iodonium dicollidine perchlorate
IR	infrared
IRIS	infrared ion spectroscopy
IRC	intrinsic reaction coordinate
J	coupling constant
KIE	kinetic isotope effect
KS-MO	Kohn-Sham molecular orbital theory
LC-MS	liquid chromatography mass spectrometry
LG	leaving group
LOS	lipooligosaccharides
LTQ	linear trap quadropole
LUMO	lowest unoccupied molecular orbital

LRP	long-range participation
Lyx	lyxose
M	molar
m	multiplet
M.	*Mycobacterium*
m.s.	molecular sieves
MS^2	tandem-mass spectrometric
m/z	mass over charge ratio
min	minute(s)
Man	mannose
ManA	mannuronic acid
Me	methyl
MFE	monofluoroethanol
MM	molecular mechanics
M.S.	molecular sieves
Nap	2-methylnaphthyl
NBS	*N*-bromosuccinimide
NIS	*N*-iodosuccinimide
NGP	neighboring group participation
NMR	nuclear magnetic resonance
NOESY	nuclear Overhauser effect spectroscopy
Nuc	nucleophile
p	*para*
P	protection group
PC	product complex
PCM	polarizable continuum model
Ph	phenyl
PMB	4-methoxybenzyl
ppm	parts per million
q	quartet
qd	quartet of doublets
QM	quantum mechanics
RC	reaction complex
R_f	retention factor
Rib	ribose
RRV	relative reactivity value
rxn	reaction
s	singlet
S	skew boat
sat.	saturated
SCF	self-consistent field
S_N1	uni-molecular nucleophilic substitution
S_N2	bi-molecular nucleophilic substitution
SSIP	solvent-separated ion pair
SAR	structure-activity-relationships
t	triplet
t	*tert*
T	twist
tg	*trans-gauche*
TBAF	tetrabutylammonium fluoride
TBAI	tetrabutylammonium iodide
TBS	*tert*-butyldimethylsilyl
TBDMS	*tert*-butyldimethylsilyl
TBDPS	*tert*-butyldiphenylsilyl
TES	triethylsilyl
TEMPO	2,2,6,6-tetramethylpiperidine 1-oxyl
TFA	trifluoroacetic acid
TFE	trifluoroethanol
Tf	triflyl; trifluoromethanesulfonyl
THF	tetrahydrofuran
TIPS	tri-*iso*-propylsilyl
TLC	thin layer chromatography
TMEDA	tetramethylethylenediamine
TMS	trimethylsilyl
TOCSY	total correlation spectroscopy
Tol	tolyl; 4-methylphenyl
TPP	triphenylphosphine
TPPO	triphenylphosphine oxide
Trt	trityl; triphenylmethyl
Ts	tosyl; 4-methylbenzene-1-sulfonyl
TS	transition state
td	triple doublet
tt	triple triplet
TPAP	tetrapropylammonium perruthenate
TTBP	2,4,6-tri-*tert*-butylpyrimidine
UDP	uridine diphosphate
UV	ultraviolet
VT	variable temperature
Xyl	xylose
YerA	yersiniose A
ZORA	zeroth order regular approximated
ZPE	zero-point energy