Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Gas-phase structure and reactivity of the keto tautomer of the deoxyguanosine radical cation

Linda Feketeová,*[a,b,c] Bun Chan,*[b,d] George N. Khairallah,[a,b] Vincent Steinmetz,[e] Philippe Maitre,[e] Leo Radom[b,d] and Richard A. J. O'Hair*[a,b]

[a] *School of Chemistry and Bio21 Institute of Molecular Science and Biotechnology, The University of Melbourne, 30 Flemington Road, Parkville, VIC, 3010, Australia. E-mail: rohair@unimelb.edu.au*

[b] *ARC Centre of Excellence for Free Radical Chemistry and Biotechnology, Australia.*

[c] *Université de Lyon, 69003 Lyon, France; CNRS/IN2P3, UMR5822, Institut de Physique Nucléaire de Lyon, 69622 Villeurbanne, France. E-mail: l.feketeova@ipnl.in2p3.fr*

[d] *School of Chemistry, University of Sydney NSW, 2006, Australia. E-mail: bun.chan@sydney.edu.au, radom@chem.usyd.edu.au*

[e] *Laboratoire de Chimie Physique, Université Paris Sud, 15, Avenue Jean Perrin, Orsay Cedex, 91405, France. E-mail: philippe.maitre@u-psud.fr*

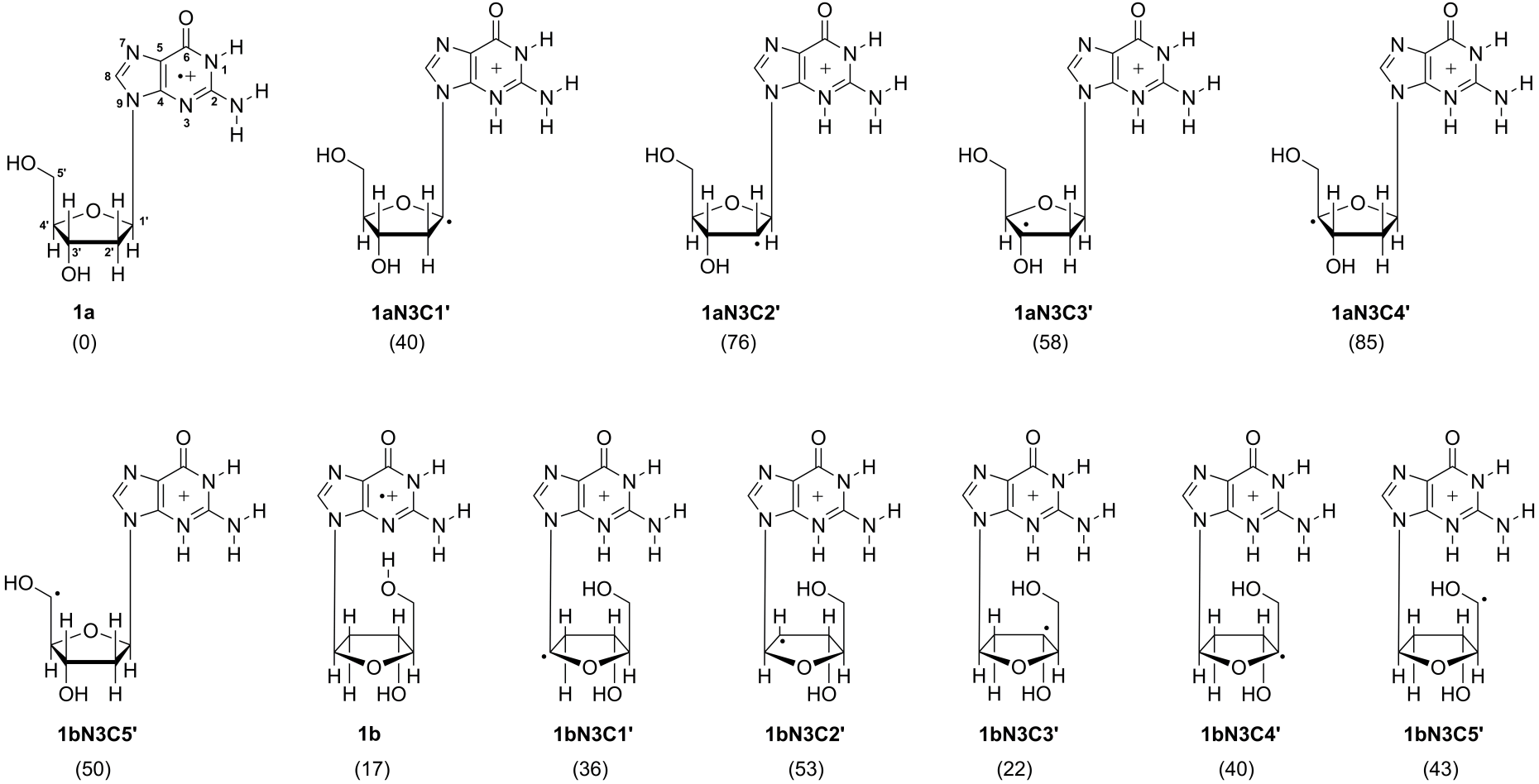


Figure S1: M06-2X/6-311+G(3df,2p) calculated minimum energy structures for the anti (**1a**) and syn (**1b**) keto tautomers of the deoxyguanosine radical cation together with their distonic isomers arising from H-atom transfer from the sugar ring to the N3 position of the nucleobase. The numbering of these distonic ions reflects the atom sites defined in **1a**. Free energies (ΔG) (M06-2X/6-311+G(3df,2p), 298 K, kJ mol^{-1}), calculated relative to the most stable keto isomer (**1a**) are given in parentheses.

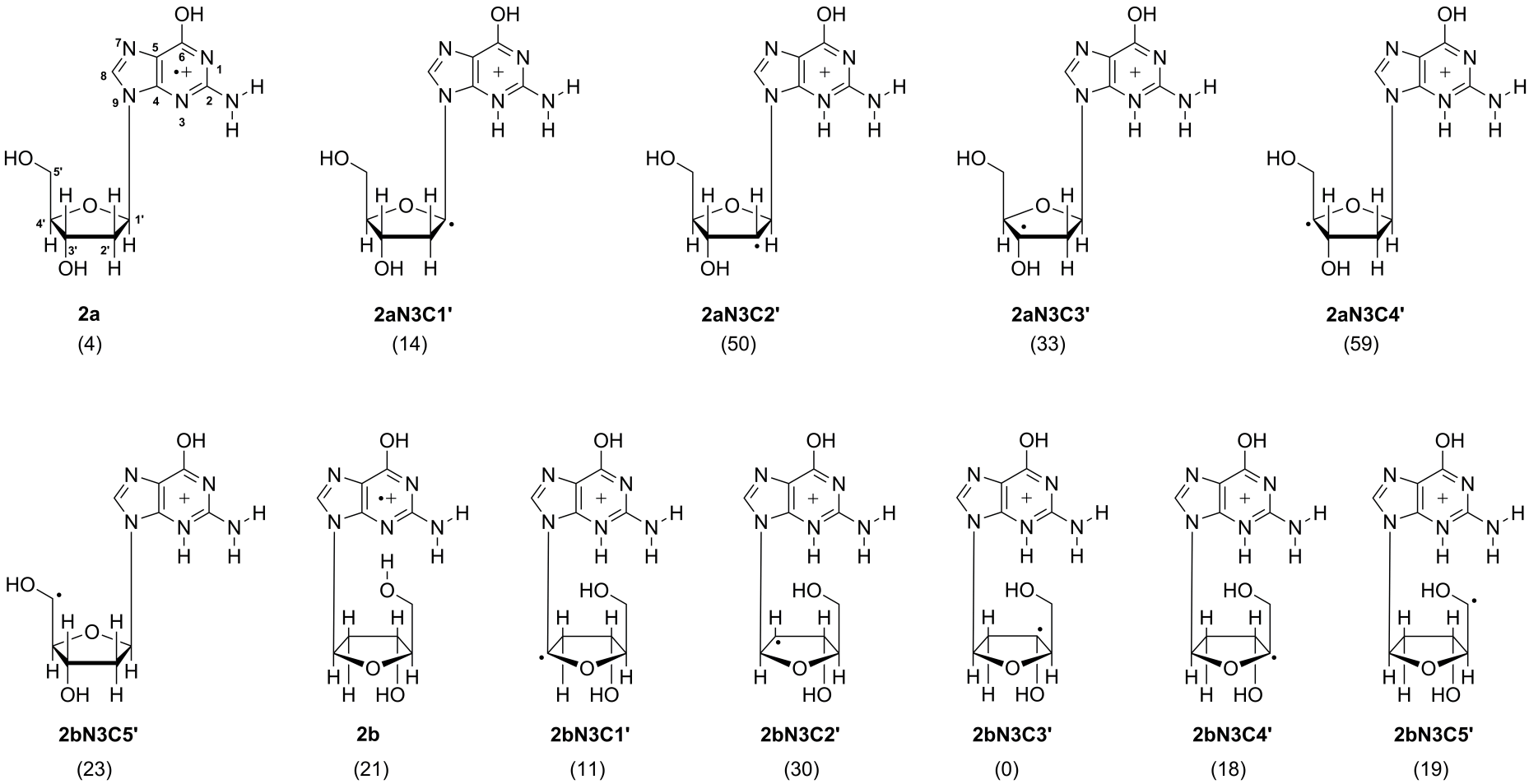


Figure S2: M06-2X/6-311+G(3df,2p) calculated minimum energy structures for the anti (**2a**) and syn (**2b**) enol tautomers of the deoxyguanosine radical cation together with their distonic isomers arising from H-atom transfer from the sugar ring to the N3 position of the nucleobase. The numbering of these distonic ions reflects the atom sites defined in **1a**. Free energies (ΔG) (M06-2X/6-311+G(3df,2p), 298 K, kJ mol^{-1}), calculated relative to the most stable keto isomer (**1a**) are given in parentheses.

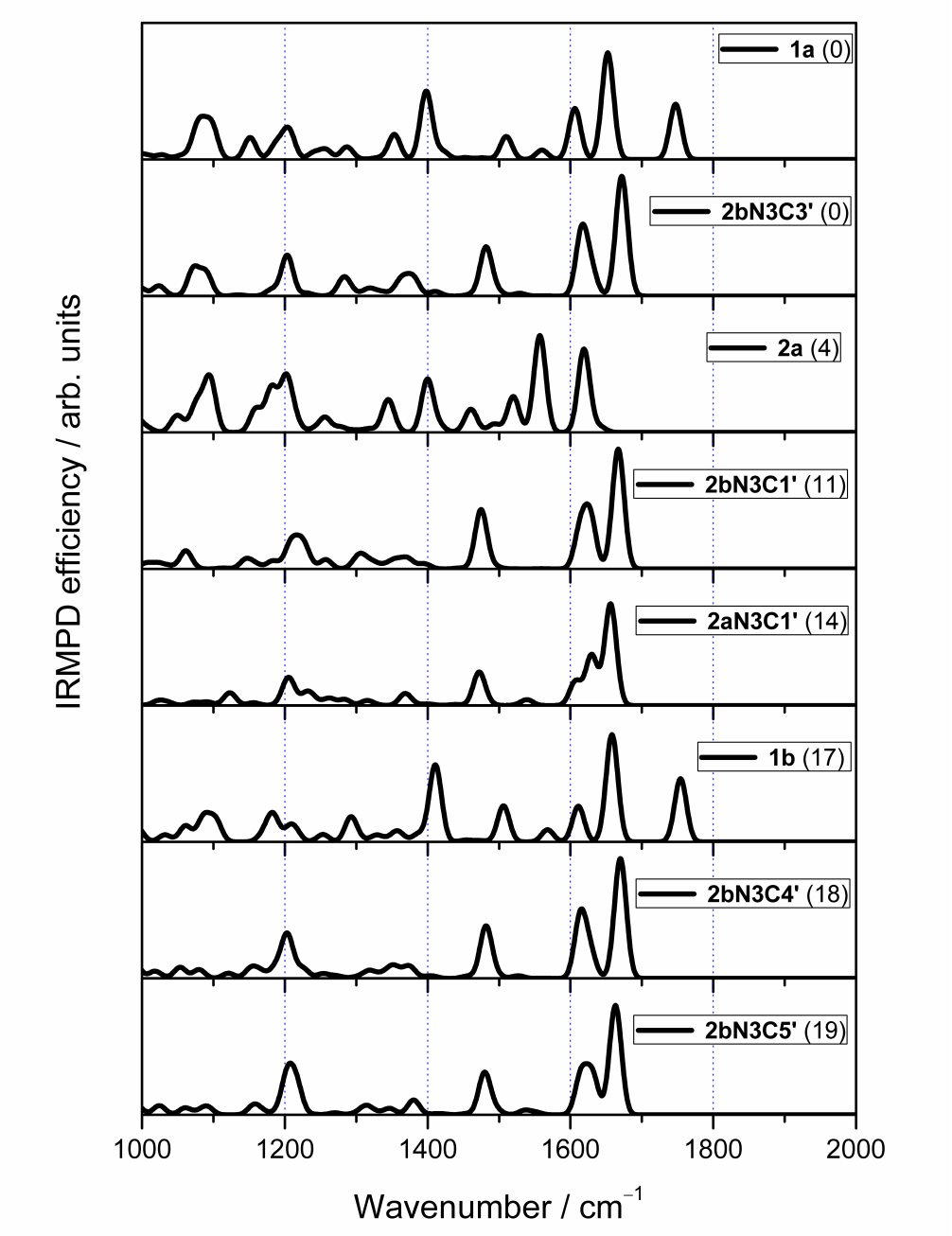


Figure S3: Theoretical B3-LYP/6-31+G(d,p) infrared spectra of isomers of deoxyguanosine radical cation in order of increasing relative free energy (M06-2X/6-311+G (3df,2p), 298 K, kJ mol^{-1}) given in parentheses.

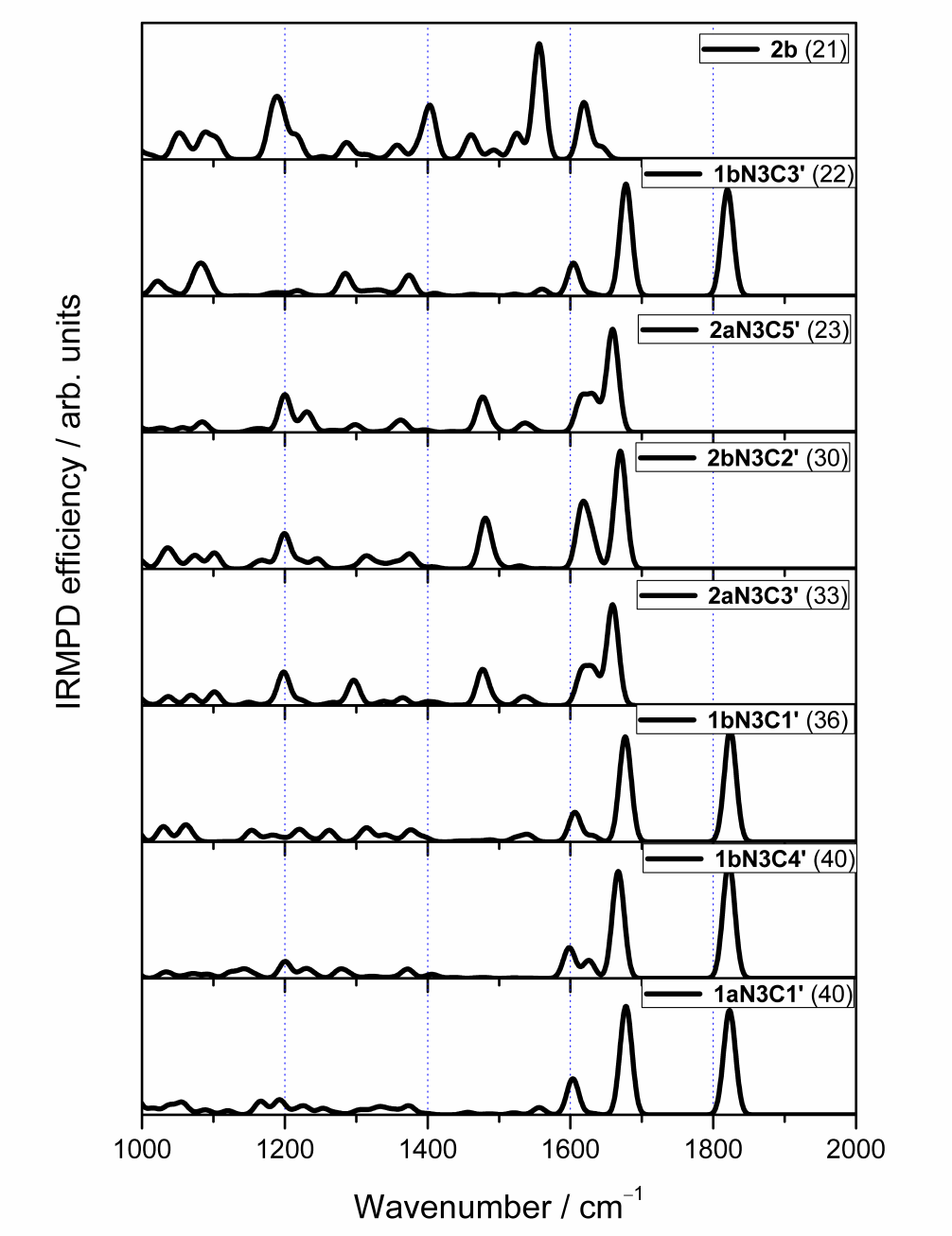


Figure S3 (continued): Theoretical B3-LYP/6-31+G(d,p) infrared spectra of isomers of deoxyguanosine radical cation in order of increasing relative free energy (M06-2X/6-311+G(3df,2p), 298 K, kJ mol^{-1}) given in parentheses.

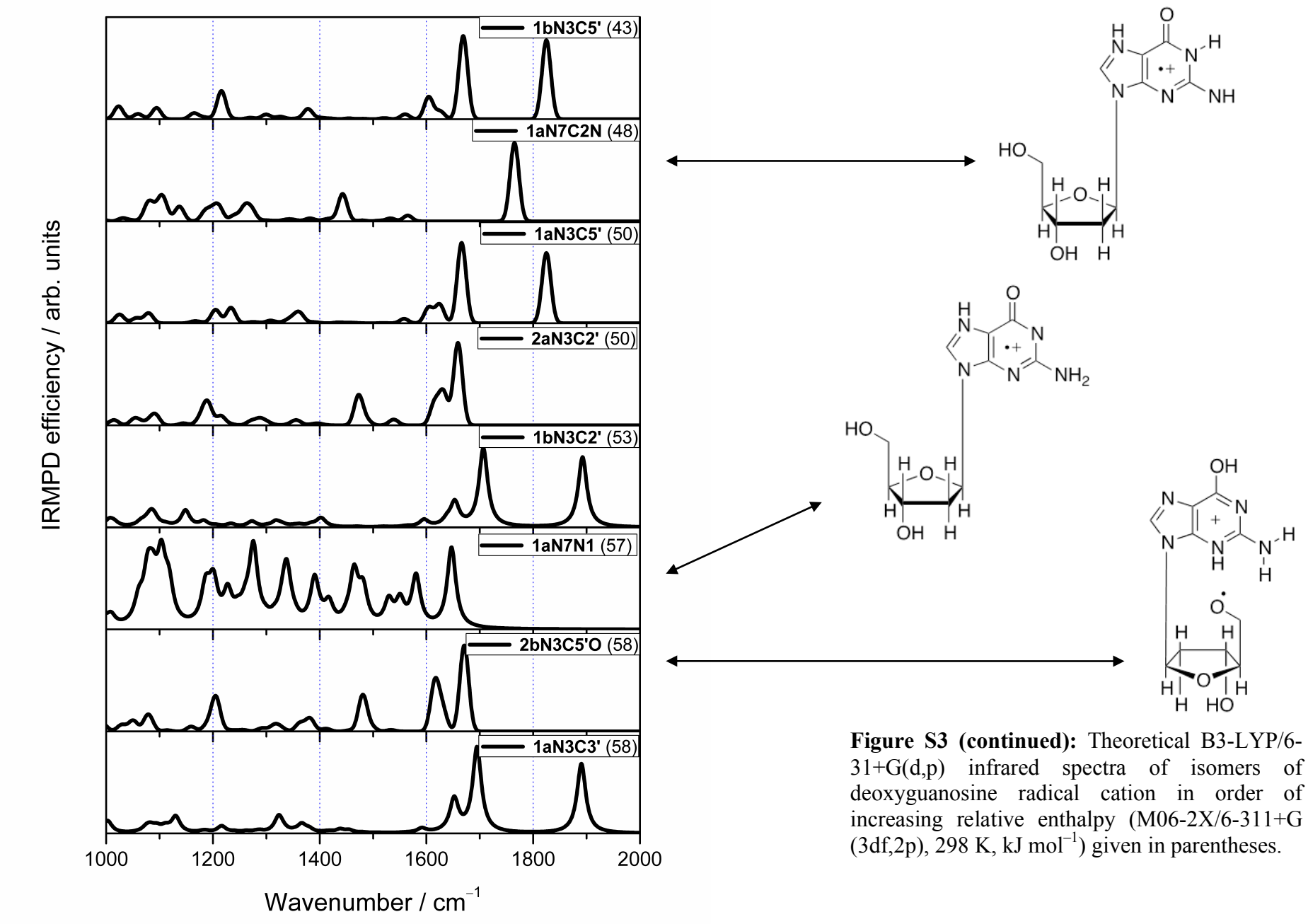
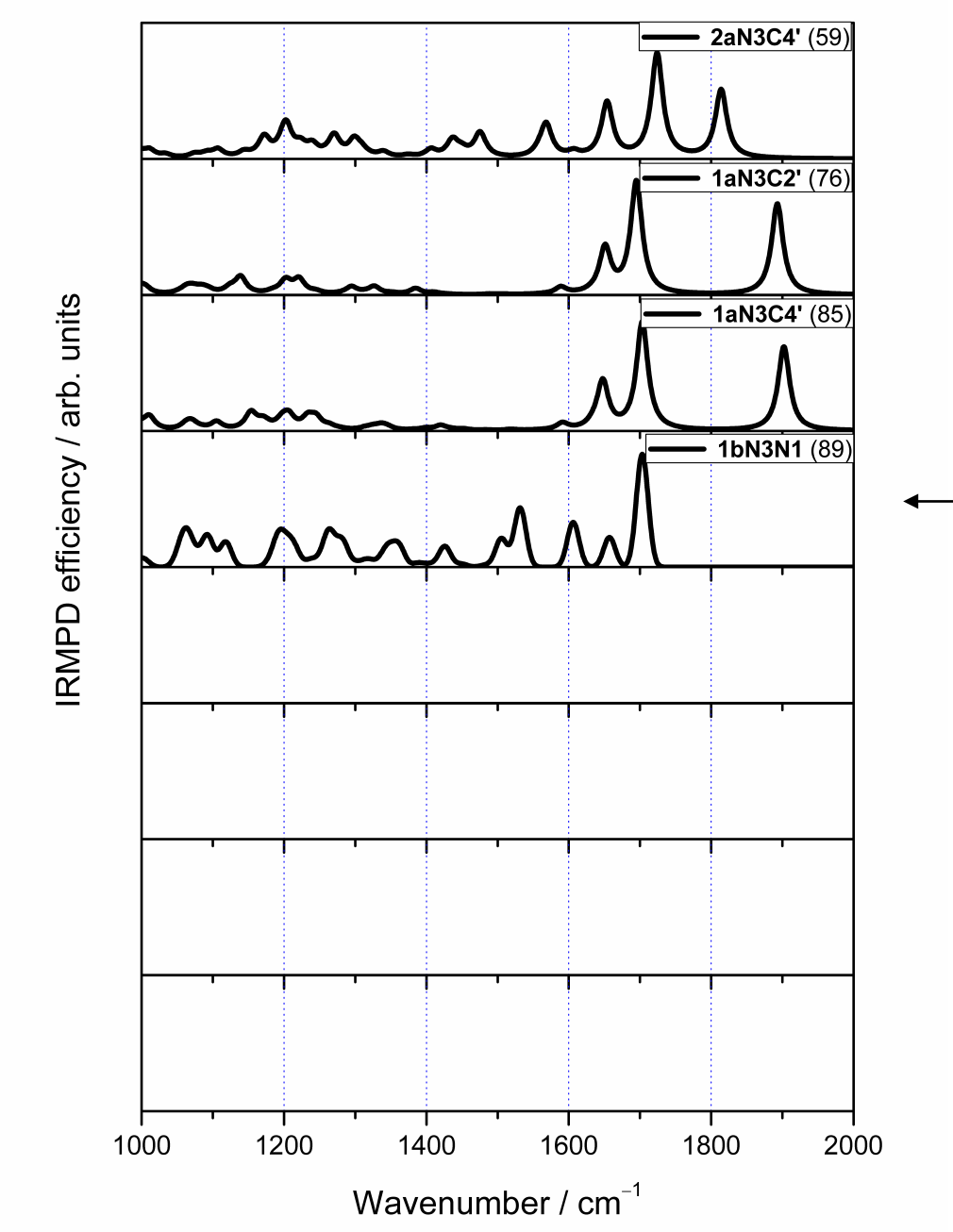


Figure S3 (continued): Theoretical B3-LYP/6-31+G(d,p) infrared spectra of isomers of deoxyguanosine radical cation in order of increasing relative enthalpy (M06-2X/6-311+G (3df,2p), 298 K, kJ mol^{-1}) given in parentheses.



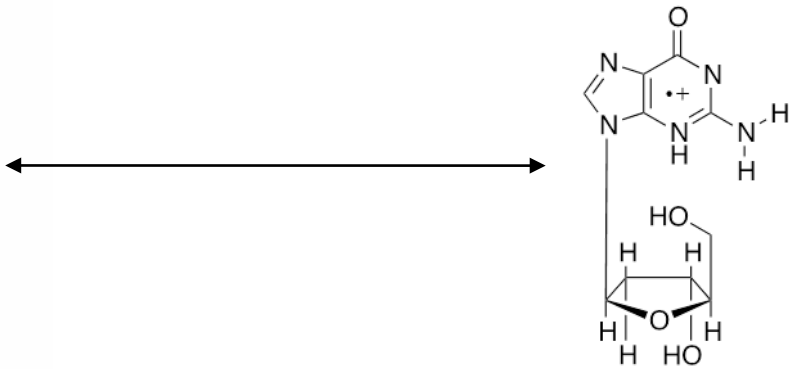


Figure S3 (continued): Theoretical B3-LYP/6-31+G(d,p) infrared spectra of isomers of deoxyguanosine radical cation in order of increasing relative free energy (M06-2X/6-311+G (3df,2p), 298 K, kJ mol^{-1}) given in parentheses.

Description	Experimental frequency	1a frequency (intensity)
CH_2 rock	1110	1076 (105)
CN and CO st.		1084 (84)
CC st.		1089 (46)
CO st.		1099 (154)
CN st.		1152 (113)
COH bend	1200	1207 (132)
CC st.	1275	1258 (50)
Ring def		1287 (64)
CH & NH bend	1372	1353 (63)
C-NH_2 st.		1355 (66)
Ring def. & CH bend		1398 (311)
Ring def. (C(2)N(3) st.)	1511	1510 (118)
NH_2 sciss.	1595	1606 (262)
Ring def. (C(4)N(3) st.)	1640	1653 (547)
C=O stretch	1750	1748 (284)

Table S1: Assignment of experimentally-observed vibrational bands through comparison with calculated IR bands and intensities of the keto isomer **1a** of the dG radical cation. The numbers in parentheses correspond to predicted intensities in km mol^{-1}.

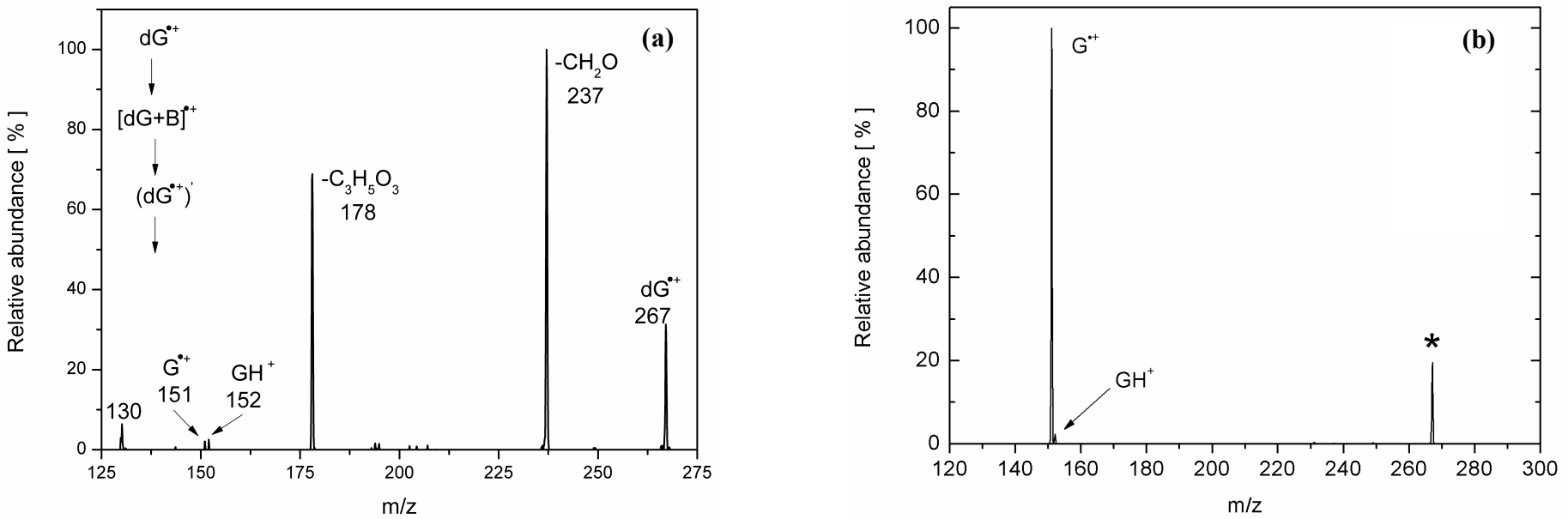


Figure S4: MS/MS CID spectrum of dG radical cation: (a) that has isomerised in the ion–molecule reactions with iPr_2NEt at 1000 ms reaction time, the formed adduct was dissociated at 20 V and the formed dG radical cation re-isolated and subjected to CID at 19 V; (b) that is formed in the ESI.

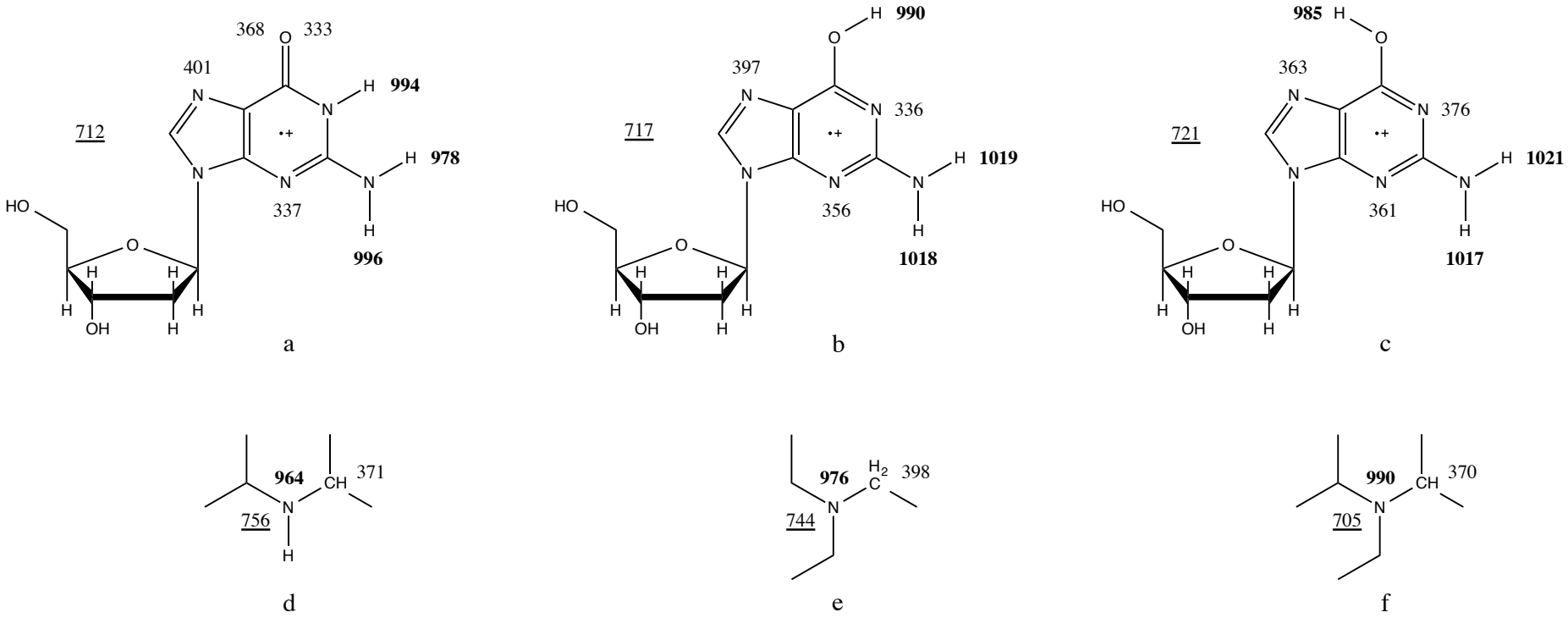


Figure S5: M06-2X/6-311+G(3df,2p) thermochemical properties (ΔH, 298 K, kJ mol^{-1}): (1) energies for hydrogen-atom abstraction by dG$^{\bullet+}$ (a–c) and BDEs for the amines (d–f), (2) **deprotonation energies for dG$^{\bullet+}$ and PAs for the amines**, and (c) electron affinities for dG$^{\bullet+}$ and IEs for the amines.

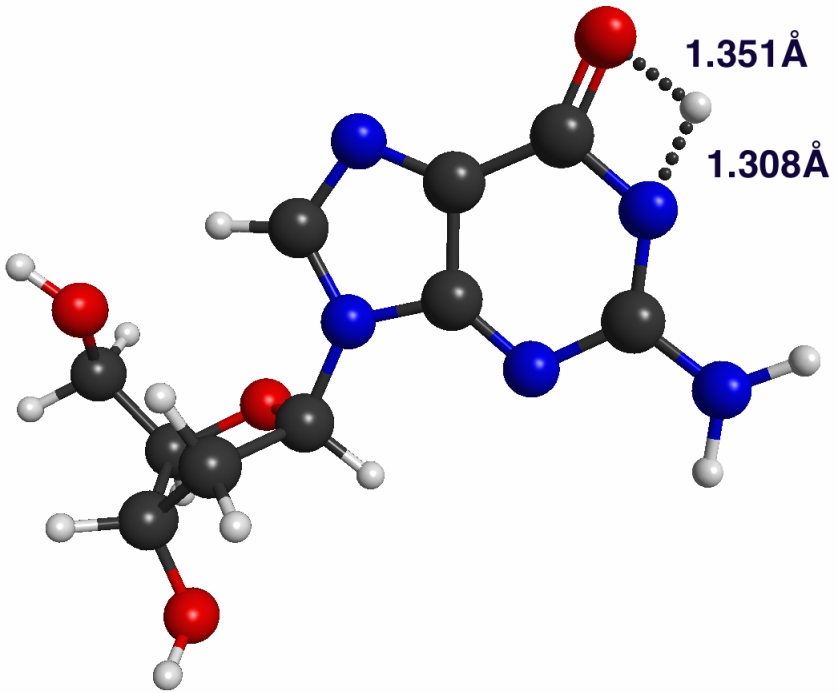


Figure S6: Transition structure for the intramolecular 1,3-shift corresponding to the keto-enol tautomerisation of $dG^{\bullet+}$.