ChemComm

This article is part of the

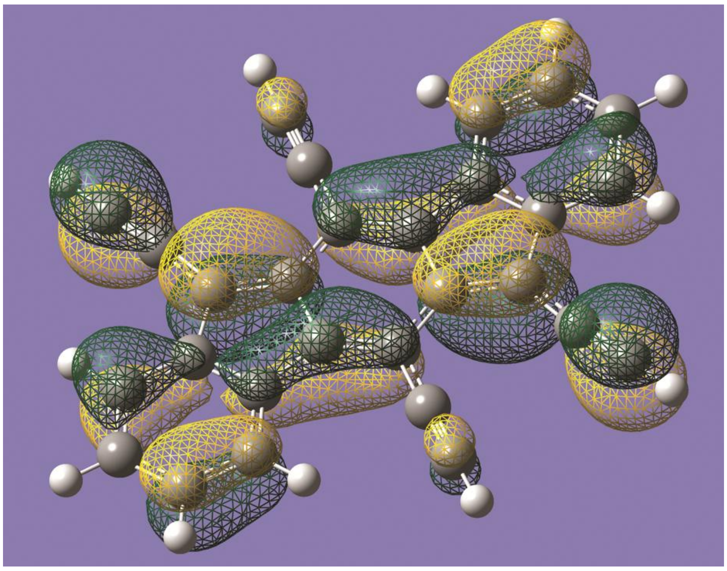
Aromaticity

web themed issue

Guest editors: Nazario Martín, Michael Haley and Rik Tykwinski

All articles in this issue will be gathered together online at

www.rsc.org/cc/aroma



ChemComm

Dynamic Article Links

Cite this: *Chem. Commun.*, 2012, **48**, 6791–6793

www.rsc.org/chemcomm

COMMUNICATION

A rigid donor–acceptor daisy chain dimer†‡

Dennis Cao,[ab] Cheng Wang,[a] Marc A. Giesener,[a] Zhichang Liu[a] and J. Fraser Stoddart*[ab]

Received 6th April 2012, Accepted 30th April 2012

DOI: 10.1039/c2cc32499g

A functionalised cyclobis(paraquat-*p*-phenylene) attached by a rigid linker to a tetrathiafulvalene unit, which is incapable of self-complexation, forms preferentially a [*c*2]daisy chain which undergoes rapid disassociation and reassociation on the ^{1}H NMR time-scale above room temperature.

Artificial molecular muscles and actuators have become a source of interest in recent years because of their incorporation into nanoelectromechanical systems (NEMS)[1] in order to transduce nanoscale molecular motions into macroscopic movements.[2] Elastomers,[3] conducting polymers,[4] and carbon nanotubes,[5] capable of actuation, have all been a part of this interest. Simultaneously, mechanically interlocked molecules[2] (MIMs) which mimic protein filaments in biological systems, have generated attention since the discrete relative movements of their components can be controlled by a number of different stimuli. To this end, in addition to electrochemically-stimulated doubly bistable [3]rotaxanes,[6] both acid–base[7] and chemically[8b] actuated bistable [*c*2]daisy chains have been introduced. The latter have been designed and synthesised around metal–ligand coordination,[8] hydrogen bonding,[7,9] hydrophobic,[10] and π-donor/acceptor interactions,[11] as the sources of their mutual recognition units. More often than not, however, daisy chain monomers self-assemble in solution to give[10c–d,11] a mixture of linear and cyclic oligomers, depending on the concentration of the monomer.

In the case of donor–acceptor-based daisy chains, there have been numerous attempts to attach flexible donating units to the electron-deficient cyclobis(paraquat-*p*-phenylene)[12] ($CBPQT^{4+}$) ring. These monomers, however, have shown[13] a strong tendency to self-complex, rather than form higher order superstructures, no doubt as a consequence of the considerable entropic penalty associated with the generation of supramolecular polymers, be they cyclic or acyclic. In order to circumvent self-complexation, we envisage that the use of a rigid spacer of an appropriate length between the donor and the $CBPQT^{4+}$ ring might eliminate the possibility for intramolecular interactions altogether, thus favouring the formation of daisy chains. Herein, we report the synthesis and characterisation of a daisy chain-forming compound $\mathbf{1}^{4+}$ which consists (Fig. 1) of a tetrathiafulvalene (TTF) unit joined by rigid aromatic linkers to a $CBPQT^{4+}$ ring for the all but exclusive construction of a donor–acceptor [*c*2]daisy chain. Several important considerations were taken into account in designing $\mathbf{1}^{4+}$, including (i) the rigidity of the linker which was enforced by a phenylacetylene-containing spacer whose length (11.6 Å) is greater than the length (9.9 Å) of the $CBPQT^{4+}$ cavity, ensuring that self-complexation cannot occur, (ii) the choice of TTF as the electron-rich donor since previously we have noted[14] that 1-ethynyl-5-hydroxynaphthalene derivatives have a low binding affinity for the $CBPQT^{4+}$ ring, and (iii) the use of a phthalimide linker in place of one of the xylylene units in the $CBPQT^{4+}$ ring because substituents attached to the imide nitrogen are oriented at right angles to the mean plane of the $CBPQT^{4+}$ ring, a situation which maintains a plane of symmetry in a perpendicular direction, thus avoiding the generation of isomeric [*c*2]daisy chains.

The synthesis (Scheme 1) of **1**·4PF$_6$ begins[15] with a Diels–Alder reaction between 2,5-dimethylfuran and maleic anhydride. Subsequent elimination of H_2O from the adduct under strongly acidic conditions yields the anhydride **2** which, when condensed with 4-iodoaniline, yields **3**. Dibromide **4**, generated by the NBS bromination of **3**, was hydrolysed to afford the diol **5** in order to "protect" the benzylic bromides during the subsequent Sonogashira coupling. The TTF derivative **6**[16] was then coupled to **5** to yield the intermediate **7**. Since standard PBr_3 bromination to regenerate the dibromide proved to be too harsh, mesylation of the diol followed by chloride substitution was used to generate the dichloride **8** which was

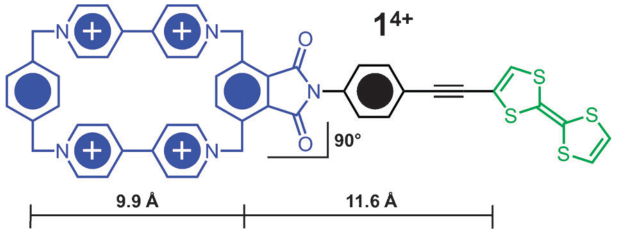


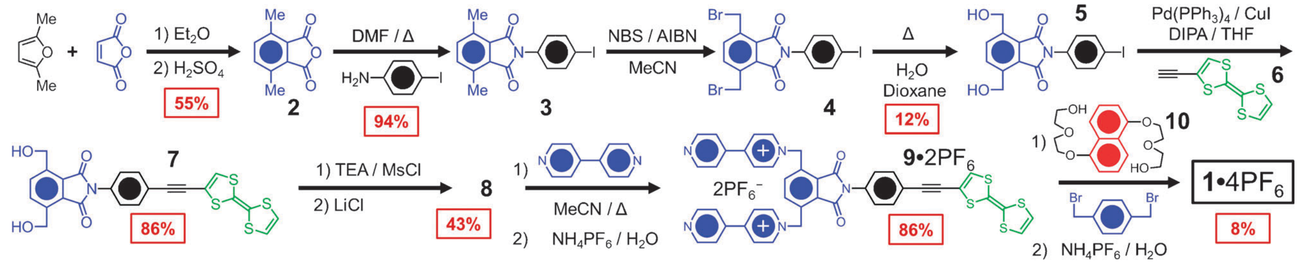
Fig. 1 The structural formula of $\mathbf{1}^{4+}$ which contains a TTF unit linked to a $CBPQT^{4+}$ ring by means of a phenylacetylene spacer.

[a] *Center for the Chemistry of Integrated Systems, Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA. E-mail: stoddart@northwestern.edu; Fax: (+1)-847-491-1009; Tel: (+1)-847-491-3793*

[b] *NanoCentury KAIST Institute and Graduate School of EEWS (WCU), Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong Dong, Yuseong Gu, Daejeon 305-701, Republic of Korea*

† This article is part of the *ChemComm* 'Aromaticity' web themed issue.

‡ Electronic Supplementary Information (ESI) available: Synthesis and characterization. See DOI: 10.1039/c2cc32499g



Scheme 1 Synthesis of $1{\cdot}4PF_6$.

reacted in MeCN with an excess of 4,4′-bipyridine to yield $\mathbf{9}{\cdot}2PF_6$ after counterion exchange. Finally, 1,4-bis(bromomethyl)-benzene was reacted with $\mathbf{9}{\cdot}2PF_6$ in the presence of template **10** to yield $\mathbf{1}{\cdot}4PF_6$ after counterion exchange and purification by high-performance liquid chromatography. High resolution electrospray ionization mass spectrometry of a 3 mM solution of $\mathbf{1}{\cdot}4PF_6$ revealed peaks at m/z = 1326.0789 and 2797.1162 Da, corresponding to the loss of one PF_6^- counterion from the monomer and dimer of $\mathbf{1}^{4+}$, respectively.

UV-Vis spectrophotometric investigations on a model TTF compound (**S1**‡) and $CBPQT^{4+}$ ($\mathbf{S2}^{4+}$‡) confirm that the TTF units functionalized with a rigid linker bind to the $CBPQT^{4+}$ ring. Indeed, when handling $\mathbf{1}{\cdot}4PF_6$, it was noticeable immediately that the colour of the solution is dependent on the concentration (Fig. 2) and the temperature. At higher concentrations, the green colour resulting from the charge transfer (CT) between TTF and $CBPQT^{4+}$ persists while, at lower concentrations, the yellow colour corresponding to a characteristic absorption band appears to dominate. A serial dilution of a solution of $\mathbf{1}{\cdot}4PF_6$ in MeCN from 2.7 mM down to 0.1 mM reveals (see SI‡) a CT band at 780 nm for the interaction between TTF and the $CBPQT^{4+}$ ring. The intensity of the band decreases as the concentration is lowered. Applying the Benesi–Hildebrand method (see SI‡) reveals a non-linear relationship between the inverse concentration and the inverse change in absorption intensity, an observation which suggests that the formation of the CT complex is most likely the result of dimerisation rather than as a consequence of self-complexation or oligomerisation.

The equilibrium (Fig. 3a) between the monomer and dimeric [*c*2]daisy chain can be followed by variable temperature (VT) ^1H NMR spectroscopy. At low temperatures, relatively sharp resonances corresponding to the cyclic dimer can be observed. With the assistance of ^1H-^1H-*g*-DQF-COSY and ^1H-^1H ROESY NMR (see SI‡), the resonances for all the protons in $\mathbf{1}^{4+}$ can be assigned (Fig. 3b) at 233 K. The resonances corresponding to the TTF protons are shifted upfield and well separated from each other, while the peaks for the methylene protons closest to the phthalimide unit separate into an AX system. We hypothesize that this AX system is a result of the stable nature of the [*c*2]daisy chain at low temperatures where the imide functionality sits exclusively on one side of the $CBPQT^{4+}$ face, imposing diastereotopism upon the H_{MTD} protons on opposite sides of the $CBPQT^{4+}$ ring. As a consequence of the sidedness of the $CBPQT^{4+}$ ring in the dimeric [*c*2]daisy chain, the resonances corresponding to the bipyridinium protons, $H_{\alpha D1}$, $H_{\alpha D2}$, $H_{\beta D1}$, and $H_{\beta D2}$, as well as to the phenylene protons, H_{PBD}, also divide up into four and two sets of resonances, respectively. Upon increasing the temperature of a CD_3CN solution of $\mathbf{1}{\cdot}4PF_6$ from 233 to 323 K, changes occur (Fig. 4) in the ^1H NMR spectra. The resonances corresponding to $H_{\alpha D1}$, $H_{\alpha D2}$, $H_{\beta D1}$, $H_{\beta D2}$, and H_{PBD} coalesce between 248 and 263 K, indicating that the rotations of the pyridinium and phenylene rings become fast on the NMR time-scale. The peaks for the protons employed to probe the energy barriers for rotation, using the coalescence method, results[17] in very similar energies of activation $\Delta G^{\ddagger}$, namely 13.8–14.5 kcal mol^{-1} from the bipyridinium and phenylene protons, indicating that we are looking at a situation involving numerous probes and realizing they reflect the same mechanism—removal of TTF units from inside $CBPQT^{4+}$ rings followed by pyridinium and phenylene ring rotations. At around 293 K, whereas the H_{TTF2D} and H_{TTF3D} resonances essentially spread out into the baseline, between 293 and 323 K, some of the peaks begin to shift while the H_{TTF2D} and H_{TTF3D} resonances reappear at around 6.3 ppm, similar to the TTF resonances in the free model compound **S1**

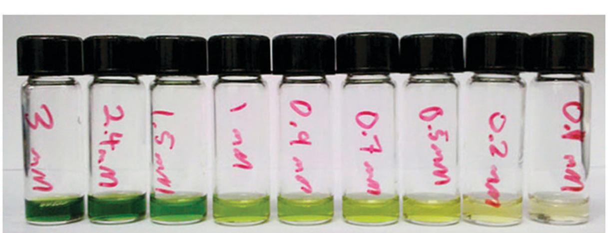


Fig. 2 Solutions of $\mathbf{1}^{4+}$ in MeCN demonstrating the change in colour as a function of concentration.

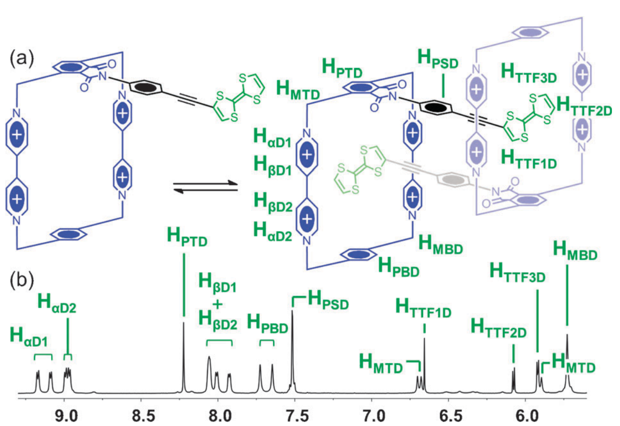


Fig. 3 (a) The proposed equilibrium between the monomer and dimer of $\mathbf{1}^{4+}$. (b) ^1H NMR spectrum (600 MHz, 2 mM, 233 K, CD_3CN) of $\mathbf{1}{\cdot}4PF_6$ and assignment of the resonances.

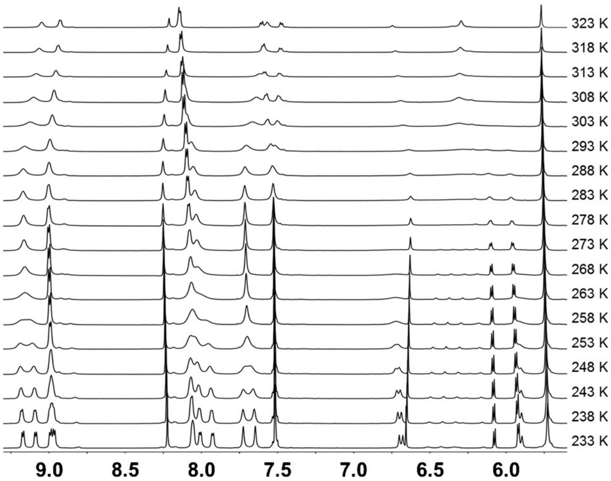


Fig. 4 VT ^{1}H NMR spectra (600 MHz, 2 mM, CD_3CN) of $\mathbf{1}^{4+}$.

(see SI‡), indicating that above room temperature there is a fast equilibrium occurring between the monomer and [*c*2]daisy chain dimer which begins to favour the free species at 323 K. Indeed, when the NMR tube was removed from the spectrometer at 323 K, the solution was yellow, and only returns to green upon cooling to room temperature. Going higher in temperature than 323 K results in the decomposition of the compound.

We have demonstrated the preferential formation of a [*c*2]daisy chain as a consequence of the rigidity in the monomer unit which rules out intramolecular interactions leading to self-complexation. The supramolecular complex undergoes rapid disassociation and reassociation on the ^{1}H NMR timescale above RT as indicated by the fact that certain protons on the $CBPQT^{4+}$ ring undergo fast exchange. The next challenge is to design and synthesize rigid donor–acceptor daisy chains with bistability.

This research is supported by the National Science Foundation (NSF) under grant CHE-0924620. D. C. and J. F. S. were supported by the WCU Program (NRF R-31-2008-000-10055-0) funded by the Ministry of Education, Science and Technology, Korea. D. C. acknowledges support from an NSF Graduate Research Fellowship.

Notes and references

1 (*a*) A. Barreiro, R. Rurali, E. R. Hernández, J. Moser, T. Pichler, L. Forró and A. Bachtold, *Science*, 2008, **320**, 775–778; (*b*) R. H. Baughman, *Science*, 2005, **308**, 63–65.
2 A. Coskun, M. Banaszak, R. D. Astumian, J. F. Stoddart and B. A. Grzybowski, *Chem. Soc. Rev.*, 2012, **41**, 19–30.
3 (*a*) Q. M. Zhang, V. Bharti and X. Zhao, *Science*, 1998, **280**, 2101–2104; (*b*) A. Buguin, M.-H. Li, P. Silberzan, B. Ladoux and P. Keller, *J. Am. Chem. Soc.*, 2006, **128**, 1088–1089; (*c*) F. Carpi, G. Gallone, F. Galantini and D. De Rossi, *Adv. Funct. Mater.*, 2008, **18**, 235–241.
4 (*a*) T. F. Otero and J. M. Sansieña, *Adv. Mater.*, 1998, **10**, 491–494; (*b*) L. Bay, K. West, P. Sommer-Larsen, S. Skaarup and M. Benslimane, *Adv. Mater.*, 2003, **15**, 310–313.
5 (*a*) R. H. Baughman, C. Cui, A. A. Zakhidov, Z. Iqbal, J. N. Barisci, G. M. Spinks, G. G. Wallace, A. Mazzoldi, D. De Rossi, A. G. Rinzler, O. Jaschinski, S. Roth and M. Kertesz, *Science*, 1999, **284**, 1340–1344; (*b*) A. E. Aliev, J. Oh, M. E. Kozlov, A. A. Kuznetsov, S. Fang, A. F. Fonseca, R. Ovalle, M. D. Lima, M. H. Haque, Y. N. Gartstein, M. Zhang, A. A. Zakhidov and R. H. Baughman, *Science*, 2009, **323**, 1575–1578.
6 B. K. Juluri, A. S. Kumar, Y. Liu, T. Ye, Y.-W. Yang, A. H. Flood, L. Fang, J. F. Stoddart, P. S. Weiss and T. J. Huang, *ACS Nano*, 2009, **3**, 291–300.
7 (*a*) J. Wu, K. C.-F. Leung, D. Benítez, J.-Y. Han, S. J. Cantrill, L. Fang and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2008, **47**, 7470–7474; (*b*) F. Coutrot, C. Romuald and E. Busseron, *Org. Lett.*, 2008, **10**, 3741–3744; (*c*) L. Fang, M. Hmadeh, J. Wu, M. A. Olson, J. M. Spruell, A. Trabolsi, Y.-W. Yang, M. Elhabiri, A.-M. Albrecht-Gary and J. F. Stoddart, *J. Am. Chem. Soc.*, 2009, **131**, 7126–7134; (*d*) P. G. Clark, M. W. Day and R. H. Grubbs, *J. Am. Chem. Soc.*, 2009, **131**, 13631–13633; (*e*) M. Hmadeh, L. Fang, A. Trabolsi, M. Elhabiri, A.-M. Albrecht-Gary and J. F. Stoddart, *J. Mater. Chem.*, 2010, **20**, 3422–3430; (*f*) C. Romuald, E. Busseron and F. Coutrot, *J. Org. Chem.*, 2010, **75**, 6516–6531.
8 (*a*) M. C. Jiménez, C. Dietrich-Buchecker, J.-P. Sauvage and A. De Cian, *Angew. Chem., Int. Ed.*, 2000, **39**, 1295–1298; (*b*) M. C. Jimenez-Molero, C. Dietrich-Buchecker and J.-P. Sauvage, *Chem.–Eur. J.*, 2002, **8**, 1456–1466; (*c*) J. Voignier, J. Frey, T. Kraus, M. Buděšínský, J. Cvačka, V. Heitz and J.-P. Sauvage, *Chem.–Eur. J.*, 2011, **17**, 5404–5414; (*d*) D.-H. Qu and H. Tian, *Chem. Sci.*, 2011, **2**, 1011–1015.
9 (*a*) P. R. Ashton, I. Baxter, S. J. Cantrill, M. C. T. Fyfe, P. T. Glink, J. F. Stoddart, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1998, **37**, 1294–1297; (*b*) S.-H. Chiu, S. J. Rowan, S. J. Cantrill, J. F. Stoddart, A. J. P. White and D. J. Williams, *Chem. Commun.*, 2002, 2948–2949; (*c*) H. Sasabe, N. Inomoto, N. Kihara, Y. Suzuki, A. Ogawa and T. Takata, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 4154–4160; (*d*) S.-H. Ueng, S.-Y. Hsueh, C.-C. Lai, Y.-H. Liu, S.-M. Peng and S.-H. Chiu, *Chem. Commun.*, 2008, 817–819; (*e*) H. W. Gibson, N. Yamaguchi, Z. Niu, J. W. Jones, C. Slebodnick, A. L. Rheingold and L. N. Zakharov, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 975–985; (*f*) B. Zheng, M. Zhang, S. Dong, J. Liu and F. Huang, *Org. Lett.*, 2012, **14**, 306–309.
10 (*a*) T. Fujimoto, Y. Uejima, H. Imaki, N. Kawarabayashi, J. H. Jung, Y. Sakata and T. Kaneda, *Chem. Lett.*, 2000, **29**, 564–656; (*b*) H. Onagi, C. J. Easton and S. F. Lincoln, *Org. Lett.*, 2001, **3**, 1041–1044; (*c*) A. Kanaya, Y. Takashima and A. Harada, *J. Org. Chem.*, 2011, **76**, 492–499; (*d*) M. Zhang, S. Li, S. Dong, J. Chen, B. Zheng and F. Huang, *Macromolecules*, 2011, **44**, 9629–9634; (*e*) N. L. Strutt, H. Zhang, M. A. Giesener, J. Lei and J. F. Stoddart, *Chem. Commun.*, 2012, **48**, 1647–1649.
11 (*a*) P. R. Ashton, I. W. Parsons, F. M. Raymo, J. F. Stoddart, A. J. P. White, D. J. Williams and R. Wolf, *Angew. Chem., Int. Ed.*, 1998, **37**, 1913–1916; (*b*) B. Zheng, F. Wang, S. Dong and F. Huang, *Chem. Soc. Rev.*, 2012, **41**, 1621–1636.
12 B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1547–1550.
13 (*a*) Y. Liu, A. H. Flood and J. F. Stoddart, *J. Am. Chem. Soc.*, 2004, **126**, 9150–9151; (*b*) M. M. Boyle, R. S. Forgan, D. C. Friedman, J. J. Gassensmith, R. A. Smaldone, J. F. Stoddart and J.-P. Sauvage, *Chem. Commun.*, 2011, **47**, 11870–11872.
14 I. Yoon, O. Š. Miljanić, D. Benítez, S. I. Khan and J. F. Stoddart, *Chem. Commun.*, 2008, 4561–4563.
15 H. Hennige, R. P. Kreher, M. Konrad and F. Jelitto, *Chem. Ber.*, 1988, **121**, 243–252.
16 J. Riedl, P. Horáková, P. Šebest, R. Pohl, L. Havran, M. Fojta and M. Hocek, *Eur. J. Org. Chem.*, 2009, 3519–3525.
17 The rate constants, k_c, at the coalescence temperatures, T_c, were determined using the approximate expression, $k_c = \pi(\Delta\nu)/(2)^{\frac{1}{2}}$, in which $\Delta\nu$ is the limiting chemical shift (in Hz) between the exchanging proton resonances. The Eyring equation, $\Delta G^{\ddagger}_{c} = -RTln(k_c\hbar/k_BT_c)$ was used to calculate the $\Delta G^{\ddagger}_{c}$ value at the lower limit of the T_c value for the (i) $H_{\alpha D1}$ ($\Delta\nu$ = 49.8 Hz, k_c = 110.6, T_c = 263 K, $\Delta G^{\ddagger}_{c}$ = 14.0 ± 0.1 kcal mol^{-1}), (ii) $H_{\alpha D2}$ ($\Delta\nu$ = 14.6 Hz, k_c = 32.5, T_c = 248 K, $\Delta G^{\ddagger}_{c}$ = 14.5 ± 0.4 kcal mol^{-1}), (iii) $H_{\beta D}$ ($\Delta\nu$ = 48.6 Hz, k_c = 108.0, T_c = 263 K, $\Delta G^{\ddagger}_{c}$ = 14.0 ± 0.1 kcal mol^{-1}), and (iv) H_{PBD} ($\Delta\nu$ = 47.5 Hz, k_c = 105.4, T_c = 258 K, $\Delta G^{\ddagger}_{c}$ = 13.8 ± 0.1 kcal mol^{-1}) resonances. See: I. O. Sutherland, *Annu. Rep. NMR Spectrosc.*, 1972, **4**, 71–235.