Torsional Motion in (*tert*-Butyl)ammonium Hemispheraplexes: Rotational Barriers and Energy of Binding

by **Emily F. Maverick***[a]), **Carolyn B. Knobler**[a]), **Saeed Khan**[a]), **James W. Canary**[b]), **Ira B. Dicker**[c]), and **Kenneth N. Trueblood**[1])

[a]) Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569, USA
(phone: 310-825-1562, fax: 310-825-7213, e-mail: maverick@chem.uda.edu)
[b]) Department of Chemistry, New York University, New York, NY 10003, USA
[c]) Bristol-Myers Squibb Company, 5 Research Parkway, Dept. 106, Wallingford CT 06492, USA

Dedicated to Professor *Jack D. Dunitz* on the occasion of his 80th birthday

The ADPs (ADPs = atomic anisotropic displacement parameters) from the single-crystal X-ray studies of nine related TBA$^+$ (TBA$^+$ = (*tert*-butyl)ammonium) hemispheraplexes are analyzed, and the results compared to the free energy of binding of this guest by the nine hosts. The lipophilic hosts (*Fig. 1*) were synthesized over a number of years, with increasing pre-organization for and specificity of binding. Structural studies for six of the complexes have been published, but the remaining three structures, including those of the strongest binders of TBA$^+$, are disordered and have only now been completed.

New area-detector data has been analyzed for the TBA$^+$ClO$_4^-$ complexes of **5** and of **8** at two temperatures, while the original data for **9** · TBA$^+$SCN$^-$ has been treated with a disorder model. In addition, improved models are presented for the complexes of **6** and **7**. Methods for assessing the precision of the ADP analyses are discussed. Although most of the structures are imprecise, the TBA$^+$ groups do demonstrate some of the characteristics of independent motion. The general trend in calculated libration amplitudes for the TBA$^+$ group suggests that the guests with the greatest free energy of binding, and the shortest distances from N$^+$ to the ligand plane, are those with the highest barriers to internal rotation.

Introduction. – In principle, single-crystal X-ray studies may yield information about the motion of rigid groups through analysis of the ADPs (ADPs = atomic anisotropic displacement parameters) routinely obtained in refinement. The ADPs were rarely published, even for precise studies, over the past 30 years or so. Now, however, the nearly universal use of standard Crystallographic Information Files (CIFs) accompanying publication makes the ADPs available to all researchers. In addition, area detectors have made data collection so rapid, and modern computer programs have made structure solution and refinement so routine, that ADP analysis for many related structures is feasible.

Previous publications have indeed shown that ADP analysis can yield mean-square libration amplitudes and rotation barriers for various strongly bonded groups [1a,b], and that the TB (TB = *tert*-butyl) moiety may be treated as a rigid group in the analysis of ADPs from precise diffraction studies [1c,d]. Rotation barriers of *ca.* 7 to 50 kJ mol^{-1} for the TB group have been estimated by this method over a range of environments and temperatures [1d].

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[1]) Deceased May 1998.

As part of the host–guest chemistry program of the *Cram* group at UCLA, the structures of a number of perching complexes of hemispherands with TBA^+ cations have been determined. The ORTEP diagrams of the complexes invariably show more-elongated ellipsoids for the three Me C-atoms in TB than for other C-atoms in the structures (*Fig. 1*). It has been our plan to compare the torsional motions about the C_t-N^+ bond, calculated from ADP analysis, in these hemispheraplexes. Would the apparent motion of the group be correlated to the binding energy of the complex, and/or to the distance of the group from the plane of the ligand atoms?

Crystal studies with anisotropic refinement have been published for the hemispheraplexes of five hosts, **1** [2], **2** [3], **3** [4], **4** [5], and **7** [6a]. Preliminary structures of the other four complexes have frequently been discussed [6], along with their chemical properties. However, the precision of the analyses of the X-ray data for many of the complexes has been a persistent problem. Some crystals have included disordered solvent and/or anions, and, for some, the choice of space group is ambiguous. In this paper, we present the newly determined structure of **5** · $TBA^+ClO_4^-$ and the structure of **8** · $TBA^+ClO_4^-$ at two temperatures. The study of complex **9** · TBA^+SCN^-, whose preliminary structure was reported [6b], is now complete. An analysis of the previously unpublished ADPs of an anisotropic refinement of **6** · $TBA^+ClO_4^-$ [7] is included, and the structure of **7** · $TBA^+ClO_4^-$ · 0.5 THF has been further refined [6a]. A summary of the ADP analyses [1b] for all nine complexes is presented.

Experimental. – Crystal data for **5** · $TBA^+ClO_4^-$, **8** · $TBA^+ClO_4^-$ at 296 K and 200 K, and **9** · TBA^+SCN^- are given in *Table 1*[2]). *Fig. 1* provides top views of the complex cations, with displacement ellipsoids for anisotropic atoms, while *Fig. 2* gives side views with atomic numbering.

All four structures were solved by direct methods and refined by full-matrix least squares. H-Atom positions were geometrically constrained, and hydrogen DPs were fixed at 1.20 or 1.50 times the equivalent U_{iso} of the attached C atom. All four structures have disordered anions. For **5** · $TBA^+ClO_4^-$, the disorder is relatively simple, one Cl-atom and 7 O-atoms, one O at full occupancy and three pairs at 0.55/0.45 occupancy. For **8** · $TBA^+ClO_4^-$ at both temp., the disorder is much more complex, as the anions are located in channels between stacks of cations. The ClO_4^- ions were refined as rigid bodies, with group displacement parameters for the O-atoms. For **8** · $TBA^+ClO_4^-$ at 200 K, several host atoms were also refined with disorder models (*Fig. 1*). Similarly, **9** · TBA^+SCN^- contains channels with disordered anions, refined as rigid groups, but the host appears to be well-ordered.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-203520–203523 for **5** · $TBA^+ClO_4^-$, **8** · $TBA^+ClO_4^-$ (296 K), **8** · $TBA^+ClO_4^-$ (200 K), and **9** · TBA^+SCN^-, resp., CCDC-203718 for **7** · $TBA^+ClO_4^-$ · 0.5 THF, and CCDC-204880 for the anisotropic refinement of **6** · $TBA^+ClO_4^-$. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax +44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Results. – The long-term goals of the *Cram* research program included chiral recognition of amino acids and the synthesis of enzyme mimics [8]. It is of interest that the N^+-H vectors in TBA^+ are invariably staggered with respect to the three Me groups, and that strong H-bonds are formed in the order urea O > ether O > methoxyaryl O, as well as pyridyl N > ether O in **2** · $TBA^+ClO_4^-$ [3], and carboxylate O^- > ether

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[2]) *Note:* Perchlorate salts of organic compounds can be explosive and should be handled in small quantities and with great caution.

Table 1. *Crystal Data for* **5** · *TBA$^+$ClO$_4^-$*, **8** · *TBA$^+$ClO$_4^-$ at Two Temperatures, and* **9** · *TBA$^+$SCN$^-$*

Parameter	**5** · TBA$^+$ClO$_4^-$	**8** · TBA$^+$ClO$_4^-$	**8** · TBA$^+$ClO$_4^-$	**9** · TBA$^+$SCN$^-$
T/K	100	296	200	128
Host *CA* Reg. No.	73522-93-7	83604-23-3		107913-64-4
Formula	$C_{34}H_{48}ClNO_{10}$	$C_{42}H_{58}ClN_7O_{10}$		$C_{44}H_{58}N_8O_6S$
F.W./g mol^{-1}	666.18	856.40		827.04
Crystal size/mm	0.4 × 0.25 × 0.20	0.4 × 0.2 × 0.2		0.42 × 0.27 × 0.27
Space group	*Pbcn*	*I*4/*m*		*I*4/*m*
a/Å	20.2332(12)	21.1495(14)	21.056(3)	21.146(4)
b/Å	20.1779(13)	21.1495(14)	21.056(3)	21.146(4)
c/Å	16.9052(10)	20.070(2)	20.130(3)	19.323(3)
$\alpha = \beta = \gamma$/deg	90.00			
V/Å^3	6901.8(11)	8977.4(12)	8925(2)	8639(2)
Z	8	8	8	8
ρ/g cm^{-3}	1.282	1.267	1.275	1.272
μ/mm^{-1}	0.167	0.148	0.149	0.132
Diffractometer	*Bruker Smart 1000* (CCD)			*Picker FACS1* (modified)
Radiation	MoK_α, 0.7107 Å			
R(F), $I > 2\sigma(I)$,	0.0551	0.0649	0.0950	0.0846
No. reflections	5743	1981	2018	2090
$wR(F)$,	0.1455	0.2586	0.3286	0.2686
No. reflections	8448	5577	5573	3533
Θ_{min}, Θ_{max}/deg	1.43, 28.32	1.36, 28.29	1.37, 28.36	1.36, 26.49
Diff. density/e$^-$ Å^{-3}	0.485, −0.394	0.400, −0.266	0.664, −0.440	0.905, −0.893

O in **1** · TBA$^+$ [2]. *Figs. 1* and *2* show that the present structures are in agreement with these trends, as was indeed deduced from the preliminary structures.

Crystals of the TBA$^+$ClO$_4^-$ complex of host **5** were first studied in 1977. The structure of the complex cation was unambiguous and was referred to in 1979 and illustrated in 1981 [9a,b] but the anion was disordered, and structural details were never published. The new data at 100 K, measured with a diffractometer with area detector on one of the original crystals, are more precise. The cation structure was confirmed, and a reasonable model for the disorder, suggested by difference maps, refined satisfactorily. The TBA$^+$ group perches on the face of the host with two methoxyaryl O-atoms, which share a bifurcated H-bond, but the two shortest NH ··· O distances involve ether O-atoms (*Figs. 1* and *2*).

The preliminary crystal study of the TBA$^+$SCN$^-$ complex of the tris(urea) host **9** [6b] was reported but structural details were not published, again because the evident disorder of the anion was difficult to model. Though partial-occupancy S-, C-, and N-atoms overlap, requiring restraints, the present model (using the original data) is reasonable; the anion makes no close contacts with the complex cation. Two conformers are possible, one with the methoxyaryl O group *syn* and the other with the group *anti* to the three urea O-atoms. The *syn* structure of the cation found in **9** · TBA$^+$ (*Fig. 2*) is consistent with the conformation of the major component of the NaBr complex of **9** in C_6D_6 solution, deduced from ^{1}H-NMR spectra [6b]. Strong NH ··· O H-bonds are formed with the three urea O-atoms.

The crystal study of **8** · TBA$^+$ClO$_4^-$ presented an entirely different dilemma. Room-temperature photographs and scans indicated an *I*-centered cell, but treatment of

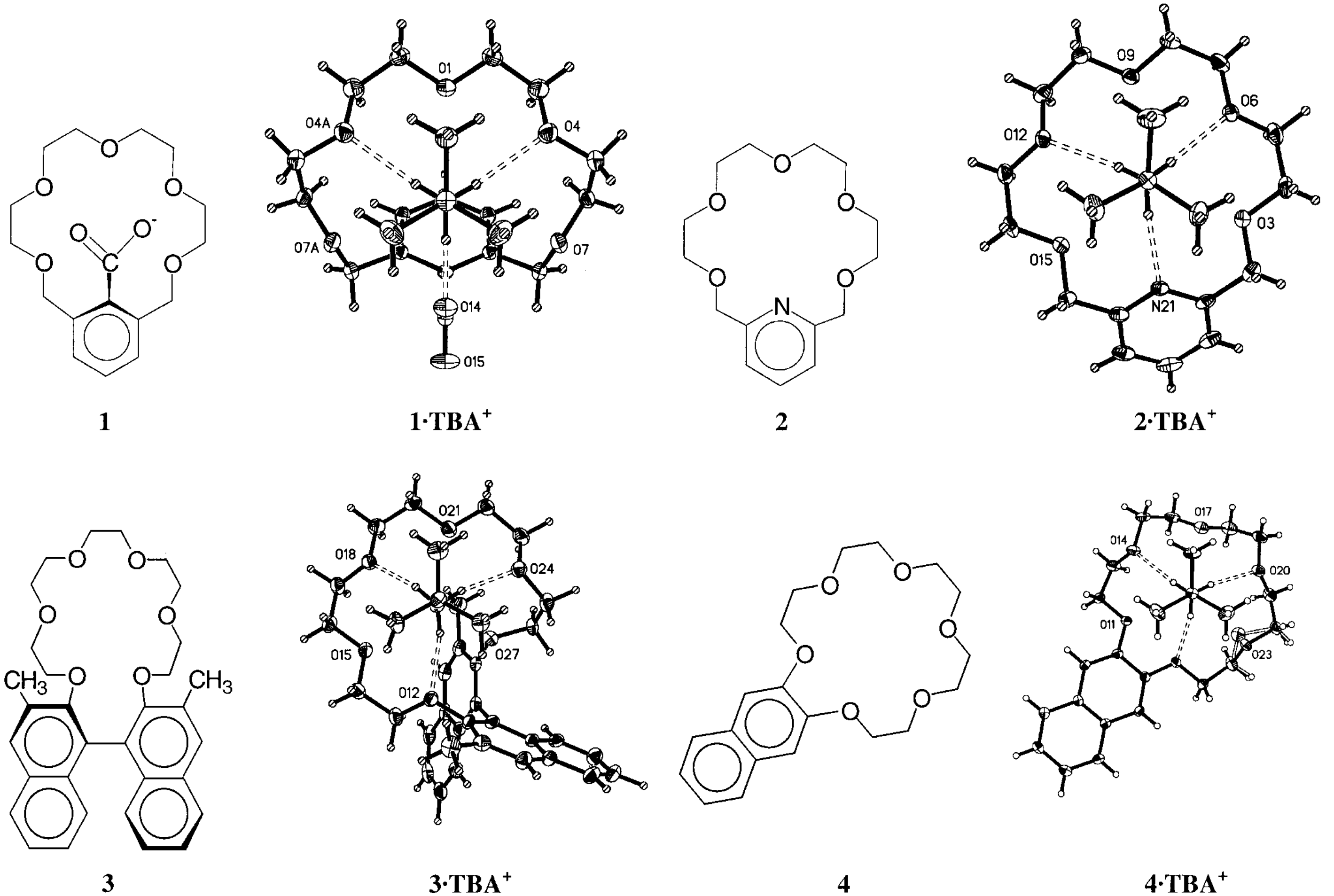
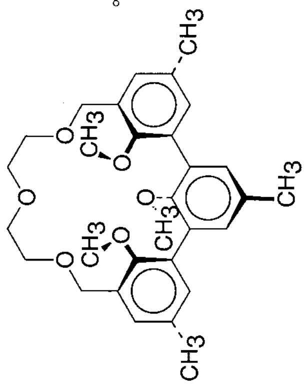


Fig. 1. *Structure diagrams of hosts* **1–9** *and ORTEP drawings of cationic complexes* (**1–9**) · *TBA*$^+$. The X-ray crystal structures of hemispheraplexes (**1–4**) · TBA$^+$ have previously been published [2–5]. Ellipsoids include 50% probability. Numbers are shown for potentially ligating O or N only; dashed lines represent H-bonds.



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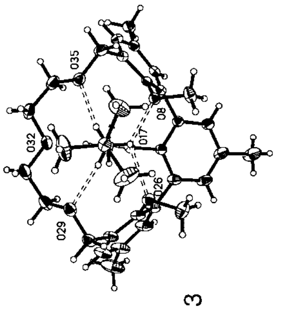
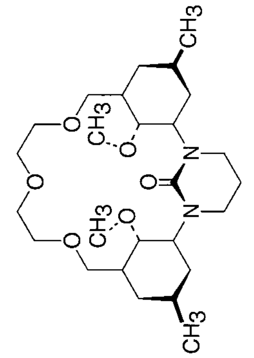


5·TBA⁺



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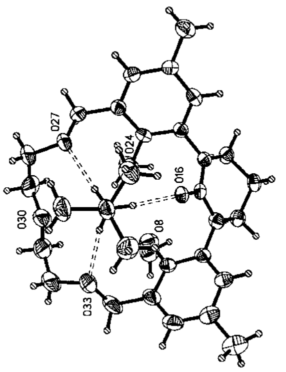
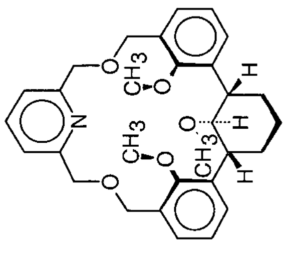


6·TBA⁺



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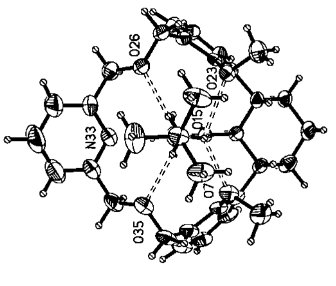
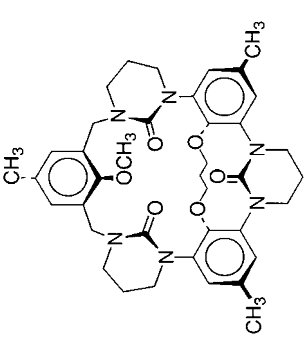


7·TBA⁺



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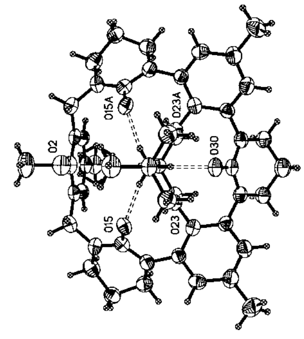
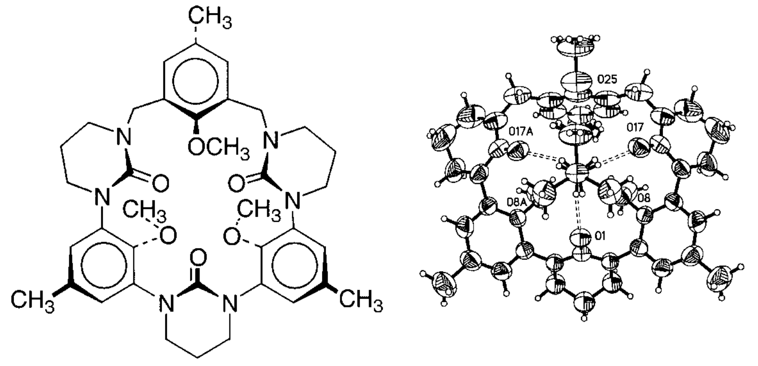


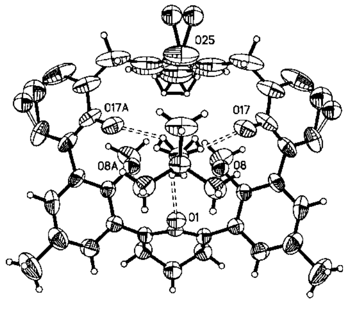
9·TBA⁺

Fig. 1 (cont.)



8

8·TBA$^+$ (296 K)



8·TBA$^+$ (200 K)

Fig. 1 (cont.)

I-centered data taken at low temperatures showed disorder of cation and anion. Different anions and solvents were tried, but no improvement was achieved. Recent area-detector data at 100 K clearly showed weak but significant reflections that did not belong to the *I*4/*m* space group. No improvement in the disorder was achieved in lower-symmetry space groups. Finally, we measured the data at room temperature. Though the anion is still disordered, the cation is much improved, and the structure refines satisfactorily. The data taken at 200 K, however, show that a phase transition is already under way (*Fig. 1*). The host is less-ordered than at room temperature, and refinement yields less-precise atomic parameters.

Drawings of the cations for all nine structures (*Fig. 1*) show elongated ellipsoids for the TBA$^+$ Me groups that suggest thermal motion. *Table 2* provides differences in MSDA (= mean square displacement amplitude) values [1b] along interatomic vectors for **5** · TBA$^+$, **8** · TBA$^+$, and **9** · TBA$^+$. For **5** · TBA$^+$, a portion of the matrix of ΔMSDA values for host atoms is also shown, and the values for the TBA$^+$ group are set apart by a horizontal line. If the ADPs are of high quality, the ΔMSDA values along bond vectors should be within *ca.* 10 pm^2 [10].

Table 3 gives ⟨sigU⟩ (= average standard uncertainties (s.u.) of U) and ⟨ΔMSDA⟩ in bonded directions, and summarizes the results of ADP analysis if TBA$^+$ is treated as a

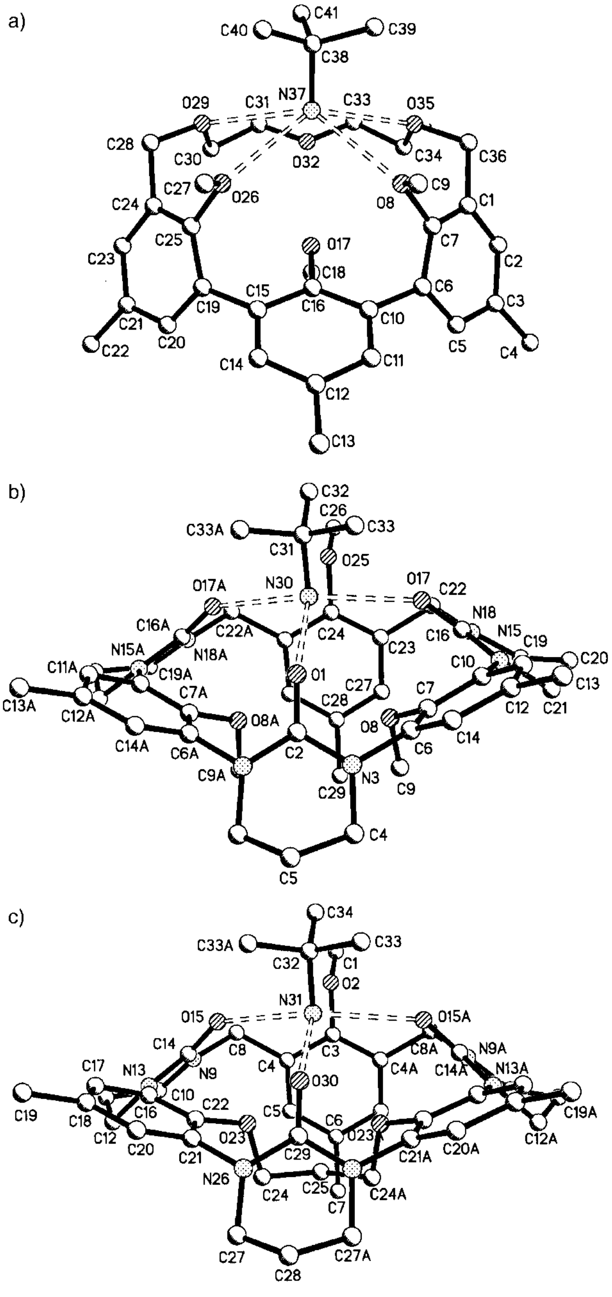


Fig. 2. *Drawings of complexes* a) **5**·TBA$^+$, b) **8**·TBA$^+$ (296 K), and c) **9**·*TBA$^+$ showing the conformations of the hosts and atomic numbering.* H-Atoms omitted for clarity; atoms represented as spheres of arbitrary radius, N-atoms dotted, O-atoms striped. Dashed 'bonds' indicate $N^+-H\cdots O$ vectors; the two such 'bonds' in **5**·TBA$^+$ to O(26) and O(8) represent a bifurcated H-bond. Some numbers for mirror-related atoms are omitted (in **8**·TBA$^+$ (296 K) and **9**·TBA$^+$).

Table 2. *Matrices of Differences in Mean-Square Displacement Amplitudes* [pm^2] *along Interatomic Lines for TBA$^+$ Groups*

5 · TBA$^+$ (100 K)

Atom	C(41)	C(40)	C(39)	C(38)	N(37)	C(36)	O(35)	C(34)	C(33)
O(32)	– 100	92	– 68	– 136	– 67	– 2	12	19	1
C(33)	210	150	105	– 28	3	– 30	– 26	3	
C(34)	316	52	91	– 28	12	– 35	– 38		
O(35)	394	56	125	11	1	1			
C(36)	373	58	63	– 15	0				
N(37)	– 10	6	19	– 56					
C(38)	28	51	16						
C(39)	– 7	– 31							
C(40)	– 1								

8 · TBA$^+$ (296 K)

Atom	C(33)	C(32)	C(31)
N(30)	21	20	– 41
C(31)	31	35	
C(32)	– 14		

8 · TBA$^+$ (200 K)

Atom	C(33)	C(32)	C(31)
N(30)	– 19	– 41	– 71
C(31)	93	– 30	
C(32)	81		

9 · TBA$^+$ (128 K)

Atom	C(34)	C(33)	C(32)
N(31)	91	54	– 43
C(32)	175	19	
C(33)	71		

rigid group librating with respect to the 'rigid' host. A rigid molecule with ADPs of high quality is expected to have all ΔMSDA values less than 10 pm^2, or at least of the order of $\langle$sigU$\rangle$ [10]. By this test, all three of the *hosts*, and the TBA$^+$ in **8**$\cdot$TBA$^+$(200 K) and **9**$\cdot$TBA$^+$, show some large deviations from rigidity. Often the N$^+$$-H\cdots$O vectors conform better to the rigidity test than do other vectors between host and guest. (This was noted for **2**$\cdot$TBA$^+$ [3], and can be seen in *Table 2* for **5**$\cdot$TBA$^+$: the ΔMSDA value for N(37)$\cdots$O(32) is -67 pm^2, compared to 1 pm^2 for N(37)$-$H$\cdots$O(35)). Therefore, the treatment was repeated with TBA$^+$ librating with respect to the three or four H-bonded ligands, in analogy to the treatment in TBA$^+$Cl$^-$ [11]. *Table 3* presents the mean-square libration amplitudes Φ^2 calculated with correlations to overall motion, [12] the threefold rotation barriers (calculated from Φ^2 and the temperature) [1d], and the corrected $C_t$$-$Me bond lengths.

Table 3. *Results of ADP Analysis with TBA$^+$ as a Rigid Group Attached to Entire Host* (*Columns 4–7*) *and as a Rigid Group Attached to H-bonded O-Atoms only* (*Columns 8–11*).

1 Host	2 T/K	3 $\langle$sigU$\rangle$/ pm^2 (rms)	4 Bonded (pm^2) $\langle\Delta$MSDA$\rangle$ (rms)	5 Libration amplitude Φ^2/deg^2	6 Barrier/ kJ mol^{-1}	7 C$-$CH$_3$ (corr.)(av.)	8 Bonded (pm^2) $\langle\Delta$MSDA$\rangle$ (rms)	9 Libration amplitude Φ^2/deg^2	10 Barrier/ kJ mol^{-1}	11 C$-$CH$_3$ (corr.)(av.)
5	100	12	17	88(6)	7.1	1.528	41	94(5)	6.5	1.530
8	296	28	56	75(23)	24	1.537	30	69(19)	26	1.538
8	200	38	75	50(20)	25	1.535	58	42(13)	30	1.535
9	128	28	76	12(10)	72	1.526	87	16(14)	51	1.528

Comments. – '*We mortals, men and women, devour many a disappointment between breakfast and dinner time...*'3)).

The precision of the ADP analyses, as shown by the large values of $\langle$sigU$\rangle$, bonded $\langle\Delta$MSDA$\rangle$, and esd of Φ^2 (in parentheses) for the TBA$^+$ complexes, is disappointingly poor. For the cations that lie on mirror planes in **8**$\cdot$TBA$^+$ and **9**$\cdot$TBA$^+$, the lack of precision is probably due in part to fewer independent parameters determining the libration amplitudes, and in part to the effect on the ADPs of the extreme disorder of the anions (*Tables 2* and *3*). As seen in *Table 3*, for **8**$\cdot$TBA$^+$, the libration amplitude Φ^2 is approximately proportional to temperature, and the esd of Φ^2 is slightly improved for **8**$\cdot$TBA$^+$ by including only TBA$^+$ and H-bonded O-atoms in the analysis. The average corrected $C_t$$-$Me bond distances of 1.53–1.54 Å provided by the librating ammonium ion model are slightly longer for the second treatment. For **5**$\cdot$TBA$^+$, corrections are *ca.* 0.0200 Å, 5 times the s.u. of the bond lengths, and for **8**$\cdot$TBA$^+$(296 K), corrections are *ca.* 0.0146 Å, 3 times the s.u. For **8**$\cdot$TBA$^+$(200 K) and **9**$\cdot$TBA$^+$, however, the corrections are 0.009 and 0.003 Å respectively, equal to or less than the s.u. The libration amplitude for **9**$\cdot$TBA$^+$ is essentially zero, the calculated barrier to rotation is high, and the thermal motion model cannot account for the ADPs in this guest.

Table 4 arranges the results of ADP analysis for all nine complexes in order of increasing free energy of binding of TBA$^+$. The columns that follow list average H-bonding distances, the 'perching' distance N$^+$ to the plane of H-bonded O or N, the

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3) *George Eliot*, 'Middlemarch'.

Table 4. *TBA^+ Complexes of Hemispherands: Binding Free Energies and Structural Parameters*

Host	T/K	ΔG^0 of Binding[a])/ kJ mol^{-1}	⟨Distance⟩/Å, N^+ to H-bonded O or N	⟨Distance⟩/Å, N^+ to plane of H-bonded O or N	No. of H-bonds	Libration amplitude of TBA^+ (Φ^2/deg^2)	⟨sigU⟩/ pm^2 (rms)	Bonded (pm^2) ⟨ΔMSDA⟩ (rms)	Barrier/ kJ mol^{-1}
9	128	– 59.8 [6b]	2.75	0.58	3	16(14)	28	87	51
8	296	– 55.2 [6b]	2.71	0.62	3	69(19)	28	30	26
6	115	– 40 [6c]	2.90	0.80	3	31(6)[b]	29	19	24
2	113	– 38 [6e]	2.99	0.95	3	31(3)[c]	13	19	23
5	100	– 32 [6a]	2.89	0.90	4	94(5)	12	41	6.5
4	115	– 28 [6a]	2.97	0.91	3	33(4)	21	17	22
3	113	– 26.8 [6f]	2.95	0.78	3	18(5)	22	78	48
7	185	– 24 [6a]	2.96	0.90	4	66(9)	22	66	17
1	120	– 18 [6d]	2.97	0.51	3	16(5)	7	4	49

[a]) Determined at 297 – 299 K, for extraction of guest from aqueous solution into $CDCl_3$ solution of host. Picrate and SCN^- were standard counterions; both give approximately the same ΔG^0 values for TBA^+ and various hosts. [8]. [b]) Parameters and esd's from anisotropic refinement, unpublished [7]. [c]) Calculated from supplementary information in [3].

number of H-bonds (four short NH $\cdots$ O distances for hosts **5** and **7**; see *Fig. 1*), and the libration amplitude for TBA^+ with esd. The next two columns describe the rigid-bond test: ⟨sigU⟩ of the ADPs and bonded ⟨ΔMSDA⟩ of the atoms included in the analysis. The only group that strictly fits the rigidity test [10] is that in **1** $\cdot$ TBA^+, though the complexes of **8** (296 K), **6**, **2**, and **4** do have bonded ⟨ΔMSDA⟩ values for TBA^+ within 2 – 3 times ⟨sigU⟩.

In the last column of *Table 4* are listed the barriers to libration about the C_t–N^+ bond, calculated from the ADP analyses. [1d] Though they should be viewed with skepticism [1], they are useful for examining the trend, since they are presumed to be independent of temperature. In general, with the exception of hosts **5**, **3**, and **1**, the calculated rotation barrier decreases with increasing binding energy. The exceptions can be rationalized as follows: for **5** $\cdot$ TBA^+, the four H-bonds are relatively long and the 'perching' distance to the plane of their O-atoms is relatively large, similar to **7** $\cdot$ TBA^+. For **1** $\cdot$ TBA^+, the binding energy is not strictly comparable to that for the other complexes because the protonated host is stabilized by a transannular H-bond [6d]. The crystals were made directly from protonated **1** and TBA, the complex is electrically neutral, the H-bond to carboxylate O^- is short (2.6 Å [2]), and, in addition, the 'perching' distance is the shortest of all of the complexes. For **3** $\cdot$ TBA^+, perhaps because the Me group attached to the binaphthyl moiety hinders rotation (*Fig. 1*), the calculated barrier appears to be anomalously high.

The best correlation of structural parameters with binding energy is the 'perching' distance, combined with the average length of the guest–host H-bond. The TBA^+ groups that lie deepest in the host, and the guests most closely surrounded by ligating atoms, are the guests in **8** $\cdot$ $TBA^+$and **9** $\cdot$ TBA^+. The increased pre-organization of the host, by replacing two aryl MeO groups with the $-OCH_2CH_2O-$ bridge, may also decrease the free energy of binding for **9** $\cdot$ TBA^+ compared to **8** $\cdot$ TBA^+. Design, synthesis, and binding studies, informed by crystal structures and CPK models, led *Cram* and co-workers to host **9** [6][8].

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