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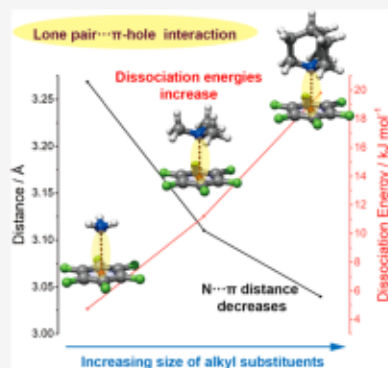
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# Rotational Spectroscopy Probes Lone Pair $\cdots\pi$ -Hole Interactions in Hexafluorobenzene-Tertiary Alkylamines Complexes

Dingding Lv, Weixing Li,\* Luca Evangelisti,\* Imanol Usabiaga, Camilla Calabrese, Assimo Maris, Sonia Melandri,\* Guanjun Wang, and Mingfei Zhou\*

**ABSTRACT:** We employed microwave spectroscopy to investigate the 1:1 complexes of hexafluorobenzene with trimethylamine and quinuclidine, respectively. These complexes exhibit a  $C_{3v}$  symmetry and are stabilized by nitrogen lone pair $\cdots\pi$ -hole interactions along the  $C_3$  axes. The N $\cdots\pi$ -center distances were determined to be 3.110(1) and 3.040(2) Å, respectively, which are shorter than that of hexafluorobenzene-ammonia at 3.2685(3) Å. Additionally, the strength of the intermolecular interaction increases with cluster size. While it was initially expected that the electron-donating effect of alkyl groups was responsible for changing the N $\cdots\pi$  interaction, the symmetry-adapted perturbation theory analysis revealed that, from hexafluorobenzene-ammonia to both hexafluorobenzene-alkylamines, electrostatic interaction actually decreases while dispersion interaction increases and becomes dominant. Interestingly, dispersion interaction decreases while electrostatic interaction increases from  $C_6F_6-N(CH_3)_3$  to  $C_6F_6-NC_7H_{13}$ . The splitting pattern of the spectra indicates hexafluorobenzene rotates freely relative to its partners along the axis of the N $\cdots\pi$ -hole interactions.

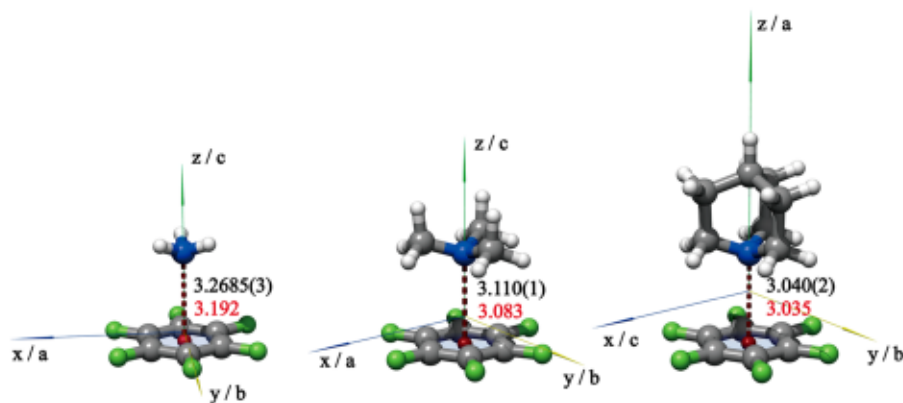


Noncovalent interactions (NCIs) are ubiquitous in nature, governing the molecular structures and thus biochemical functionalities and reactivities, such as maintaining the three-dimensional structures of biomolecules and leading molecular recognitions by the delicate balance between different NCIs on top of the covalently bound structural backbone.<sup>1–3</sup> Great effort has been devoted to the characterization of NCIs and the understanding of their nature.<sup>4–11</sup> NCIs are relatively weak compared to covalent bonds, and accurate characterization of the structure and interaction energy of NCIs experimentally is often facing significant challenges.<sup>12–14</sup> Molecular rotational spectroscopy offers a way to study NCIs on model systems under well-defined jet expansion conditions.<sup>6,7,15</sup> Rotational spectroscopy is directly related to the principal moments of inertia of the molecule including their centrifugal distortion and, therefore, is suited for analysis of geometric structures of weakly bound molecular complexes.<sup>16–19</sup> Recent rotational spectroscopic investigations have unveiled the nature of tetrel,<sup>20</sup> pnictogen,<sup>6</sup> chalcogen,<sup>15</sup> halogen,<sup>21</sup> CH $\cdots\pi$ ,<sup>22</sup> OH $\cdots\pi_{C=C}$ ,<sup>23</sup> and  $\pi$ -stacking<sup>24</sup> noncovalent interactions.

The lone pair $\cdots\pi$  hole interaction (lp- $\pi$ ) referring to the stabilizing interaction between a lone pair of electrons and an electron-poor  $\pi$  system was suggested to be responsible for the stabilization of the left-handed helix in the d(CpG) steps of Z-DNA in 1995.<sup>25</sup> The lp- $\pi$  interactions in the gas-phase clusters of halogenated ethylene and aromatic rings with water,<sup>26–28</sup> ammonia,<sup>29</sup> or formaldehyde<sup>30</sup> molecules have been studied by rotational spectroscopy. Recently, we investigated the lp- $\pi$  interaction involving the nitrogen lone pair in the hexafluor-

obenzene ( $C_6F_6$ )-ammonia ( $NH_3$ ) complex.<sup>31</sup> In this study, we report a rotational spectroscopic study on the complexes of  $C_6F_6$  with trimethylamine ( $N(CH_3)_3$ ) and quinuclidine ( $NC_7H_{13}$ ) to unravel the alkyl substituent effect on the lp- $\pi$  interactions. The fact that trimethylamine and quinuclidine are better electron donors than ammonia is widely recognized, based on the ordering of their basicity in aqueous solution, which is  $NH_3 < N(CH_3)_3 < NC_7H_{13}$ .<sup>32–34</sup> The enhanced electron-donating ability can be attributed to the alkyl groups' electron-donating effect.<sup>35,36</sup> Therefore, it is intuitively expected that the strength of lp- $\pi$  bonding would increase in the complexes of  $C_6F_6-N(CH_3)_3$  and  $C_6F_6-NC_7H_{13}$ .

Dispersion interactions were often disregarded due to the widespread belief that they are feeble.<sup>37</sup> However, as larger systems contain more pairwise interactions, dispersion increases rapidly.<sup>37,38</sup> Even in molecular dimers, dispersion interactions have been shown to be significant. For example, dispersion is as significant as electrostatic forces in stabilizing naphthol-aromatic ring complexes,<sup>39</sup> and it even dictates the interactions of diadamantyl ether-aromatics complexes.<sup>40</sup> Thus, it is crucial to comprehensively examine the interplay between

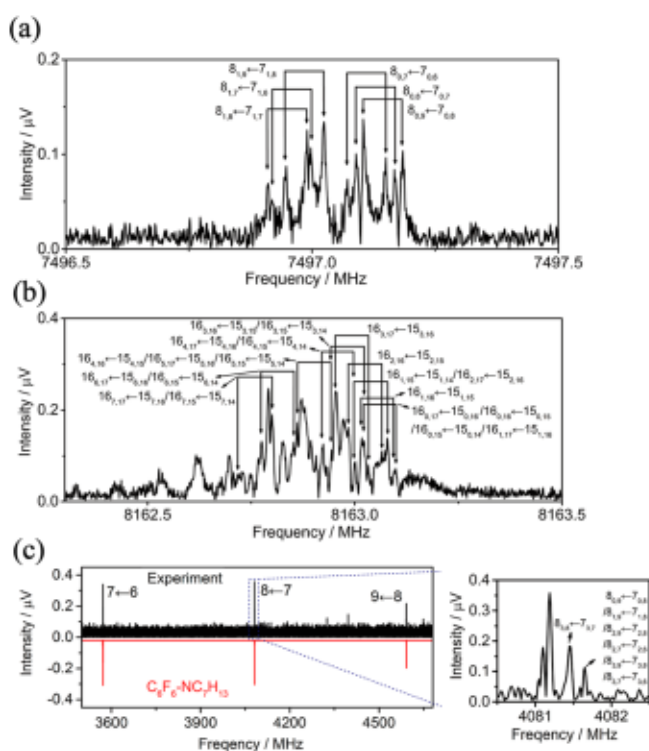


**Figure 1.** Molecular structures and N...  $\pi$ -center distances (in Å) for  $C_6F_6-NH_3$ ,  $C_6F_6-N(CH_3)_3$ , and  $C_6F_6-NC_7H_{13}$ . The distances between the nitrogen atom and the center of the aromatic ring are denoted by the red values for structures calculated at the B3LYP-D4/def2-TZVP level<sup>44</sup> and by black values for experimental results ( $r_0$ ).

different noncovalent interactions through detailed computational and experimental studies for an understanding of their role in governing the structural arrangement of biological molecules and supramolecular complexes.<sup>41–43</sup>

The theoretically predicted global minimum structures of the complexes of  $C_6F_6$  with  $N(CH_3)_3$  and  $NC_7H_{13}$ , together with  $C_6F_6-NH_3$ , are shown in Figure 1. The ammonia derivatives lie above the aromatic plane of  $C_6F_6$ , pointing their nitrogen lone pair toward the center of the ring. Their  $C_3$  symmetry axes coincide with the  $C_6$  axis of  $C_6F_6$ , resulting in a molecular  $C_{3v}$  symmetry. Consistent with the spectral characteristics of  $C_6F_6-NH_3$ ,<sup>31</sup>  $C_6F_6-N(CH_3)_3$  is also an almost spheric oblate symmetric rotor, characterized by electric dipole moment  $\mu = 1.06$  D, while  $C_6F_6-NC_7H_{13}$  is a prolate symmetric rotor with  $\mu = 1.79$  D. The calculated structural parameters can be found in the Supporting Information (Tables S1–S3).

The rotational spectra of  $C_6F_6-NC_7H_{13}$  and  $C_6F_6-N(CH_3)_3$  in the 6–18 GHz frequency range are measured using the coaxially oriented beam resonator arrangement (COBRA) Fourier Transform Microwave (FTMW) spectrometer at the University of Bologna.<sup>45–47</sup> A hyperfine structure is observed for both species, as exemplified by the transitions shown in Figure 2a,b, respectively. The spectrum of  $C_6F_6-NC_7H_{13}$  is further measured in the low-frequency range by the newly built chirped pulse FTMW Spectrometer (CP-FTMW) at Fudan University, which covers the range from 2 to 8 GHz in a single signal collection event.<sup>11,48,49</sup> The broadband spectra of  $C_6F_6-N(CH_3)_3$  in the frequency range of 6–12.5 GHz is measured using a CP-FTMW with a new solid-state amplifier. The experimental details can be found in the Supporting Information. After 1.3 million free induction decay (FID) signal accumulations, a series of spectral bunches of lines from  $C_6F_6-NC_7H_{13}$ , which are approximately equally spaced, are observed as shown in Figure 2c. This spectral signature matches that of a symmetric top. Each bunch of spectral lines contains different  $K$  components, where the quantum number  $K$  is the projection of angular momentum on the symmetry axis. Each transition is further split by the nuclear quadrupole hyperfine structure of the nitrogen atom and the internal rotation of the two moieties relative to each other in each cluster. Due to the lower resolution of the broadband spectrum than that of the narrowband spectrum, most of the transitions are blended and indistinguishable in the former.



**Figure 2.** (a)  $J = 8 \leftarrow 7$  transitions of  $C_6F_6-N(CH_3)_3$ ; (b)  $J = 16 \leftarrow 15$  transitions of  $C_6F_6-NC_7H_{13}$  measured by COBRA-FTMW spectrometer. The hyperfine components of transitions  $J_{K',F'} \leftarrow J_{K'',F''}$  are labeled by the quantum number  $F = I + J$ . Each component appears as a doublet due to the Doppler effect. (c)  $J + 1 \leftarrow J$  ( $J$  ranging from 6 to 8) transitions of  $C_6F_6-NC_7H_{13}$  measured by CP-FTMW spectrometer. The complete broadband spectra of  $C_6F_6-N(CH_3)_3$  and  $C_6F_6-NC_7H_{13}$  are available in Figure S2.

In agreement with the theoretical predictions, the rotational spectra of these complexes are assigned to the  $C_{3v}$  symmetric rotors. For  $C_6F_6-N(CH_3)_3$ , several progressions  $J + 1 \leftarrow J$  with total angular momentum quantum number  $J$  ranging from 8 to 12 are identified. The rotational spectrum of  $C_6F_6-NC_7H_{13}$  is obtained for  $J$  ranging from 6 to 21. The coupling scheme used for the labeling of the rotational transitions is  $F = I + J$ , with the nuclear spin quantum number  $I = 1$ , associated with the coupling of the nuclear quadrupole moment with the overall molecular rotation. A total of 26 transitions have been assigned

for  $C_6F_6-N(CH_3)_3$  within the 6–18 GHz range, while 123 transitions are assigned for  $C_6F_6-NC_7H_{13}$  within 2–18 GHz. The measured rotational transitions were fitted using the SPFIT program<sup>50</sup> within the  $I$  representation of Watson's  $S$  reduction Hamiltonian.<sup>51</sup> Besides the splitting of the spectral lines produced by the  $^{14}N$  nuclear spin and the Doppler effect, some additional weaker lines are observed. The frequencies of these lines are slightly red-shifted from the assigned lines, suggesting that they are associated with lower effective rotational constants. In the complex  $C_6F_6-NH_3$ , these lines have been assigned to excited torsional states that arise from the free internal rotation of  $NH_3$  with respect to  $C_6F_6$ .<sup>31</sup> For the heavier complexes of  $C_6F_6-NC_7H_{13}$  and  $C_6F_6-N(CH_3)_3$  in this study, the remaining lines from excited states are too weak and crowded to be identified (as shown in Figure 2a,b). The calculated and experimental spectroscopic constants are listed in Table 1 while all the fitted frequencies are given in

**Table 1. Experimental and Calculated Spectroscopic Parameters of  $C_6F_6-NH_3$ ,  $C_6F_6-N(CH_3)_3$ , and  $C_6F_6-NC_7H_{13}$ , Respectively**

	$C_6F_6-NH_3^a$	$C_6F_6-N(CH_3)_3$	$C_6F_6-NC_7H_{13}$
$B$ /MHz	759.6291(1) <sup>b</sup> / 768.7 <sup>c</sup>	468.5774(2)/ 471.3	255.10311(9)/ 255.7
$D_J$ /kHz	0.0910(7)	0.053(9)	0.0147(1)
$D_{JK}$ /kHz	1.899(7)	10.2 (1)	0.2387(7)
$H_{KJ}$ /Hz	-4.3(2)		0.322(4)
$D_{jm}$ /kHz	67.01(5)		
$D_{jkm}$ /kHz	11.178(1)		
$\chi_{zz}$ /MHz	-3.17(2)/-4.14	-5.43(41)/-5.91	-5.15(2)/-5.55
$N^d$	157	26	123
$\sigma^e$ /kHz	3.2	1.4	6.8

<sup>a</sup>From ref 31. <sup>b</sup>Error in parentheses in units of the last digit. <sup>c</sup>The theoretically calculated (B3LYP-D4/def2-TZVP) rotational and nuclear coupling constants. <sup>d</sup>Number of lines for fit. <sup>e</sup>Standard deviation of the fit.

Tables S4 and S5. The corresponding values for  $C_6F_6-NH_3$  are also given for comparison.<sup>31</sup> The experimental transition frequencies are in good agreement with their calculated values.

Using the theoretical optimized geometry as the initial structure of these complexes, the experimental rotational constants can be reproduced by adjusting the intermolecular distance. This adjusted result is the so-called effective structure of the ground vibrational state ( $r_0$ ).<sup>52</sup> The comparison of the theoretical and effective values is reported in Figure 1, where the errors in parentheses are given in units of the last digit. The results show that the distance between the N atom and the center of mass (CM) of  $C_6F_6$ ,  $r(N \cdots C_6F_6_{CM})$ , decreases from 3.2685(3) Å in  $C_6F_6-NH_3$ , to 3.110(1) Å in  $C_6F_6-N(CH_3)_3$ , and to 3.040(2) Å in  $C_6F_6-NC_7H_{13}$ .

The stretching force constant ( $k_s$ ) and the dissociation energies ( $E_D$ ) of the NCI can be estimated for symmetric-top complexes by approximating the complex as comprising two rigid parts. In this pseudodiatomic approximation, the stretching force constant is inversely related to the centrifugal distortion constant by the equation<sup>22,53,54</sup>

$$k_s = 128\pi^4(\mu r_{CM})^2 B^4 / (hD_J) \quad (1)$$

where  $\mu$ ,  $r_{CM}$ , and  $D_J$  are the reduced mass, the distance between the two centers of mass, and the first-order centrifugal distortion constant, respectively. The  $E_D$  is evaluated, as shown

in Table 2, by assuming a Lennard-Jones potential function, according to equation 2.<sup>55</sup>

$$E_D = 1/72k_s r_{CM}^2 \quad (2)$$

**Table 2. Distances between the Two Centers of Mass ( $r_{CM}$ ) of the Monomers from the  $r_0$  Structures, Stretching Force Constants ( $k_s$ ), and Dissociation Energies ( $E_D$ ) for  $C_6F_6-NH_3$ ,  $C_6F_6-N(CH_3)_3$ , and  $C_6F_6-NC_7H_{13}$**

	$C_6F_6-NH_3$	$C_6F_6-N(CH_3)_3$	$C_6F_6-NC_7H_{13}$
$r_{CM}$ /Å	3.325	3.439	4.320
$k_s/N m^{-1}$	5.1	11.4	13.5
$E_D$ (Exp)/kJ mol <sup>-1</sup>	4.7	11.2	21.1
$E_D$ (B3LYP-D4/def2-TZVP)/kJ mol <sup>-1</sup>	12.9	20.8	22.5

The  $E_D$  can also be predicted through quantum chemical calculations. The zero-point energy (ZPE)-corrected<sup>56</sup> values calculated at the B3LYP-D4/def2-TZVP level are also listed in Table 2 for comparison. Even though these values differ from the experimental ones, the increasing trend is in reasonable agreement with the experimental result. Both the experimental and theoretical results show that the binding energy increases with the size of the alkyl substituents. This finding is in agreement with the measured  $N \cdots \pi$ -center distances, which decreases with increasing size of the alkyl substituents.

Based on the analysis of the nuclear quadrupole coupling constants, the spectroscopic evidence of the formation of a  $lp-\pi$  interaction in these complexes can be provided using the valence p-orbital population anisotropy.<sup>57,58</sup> This analysis relies on the extended Townes-Dailey (ETD) model directly relating to the quadrupole coupling tensor.<sup>59</sup> Within the ETD model, only the valence electron population in the p-orbitals contributes to the nuclear quadrupole coupling tensor. If the nuclear quadrupole coupling principal axes and the axes of the p-orbitals coincide, the populations ( $P$ ) and the nuclear quadrupole coupling constants ( $\chi$ ) are related by equations which contain the population of the orbital and the one-electron contribution to the coupling tensor,  $\chi_0$ .<sup>60</sup> However, in the case of symmetric tops the relations reduce to a unique equation

$$\chi_{zz} = \chi_0(P_{zz} - P_{xx}) \quad (3)$$

since  $P_{xx} = P_{yy}$  and  $\chi_{xx} = \chi_{yy} = -\chi_{zz}/2$ . In particular, the experimentally derived  $\chi_0$  value for  $^{14}N$  is -11.2 MHz,<sup>61</sup> and the orientation of the  $x$ ,  $y$ , and  $z$  axes for the present systems is shown in Figure 1.

In the modified ETD model,<sup>57</sup> the  $P$ -population anisotropies  $\Delta P_{zz}$  (calculated as differences in orbital population along the  $z$  axes with respect to the average  $P_{ave}$  population) is suggested to quantify the electronic properties

$$\Delta P_{zz} = P_{zz} - P_{ave} \quad (4)$$

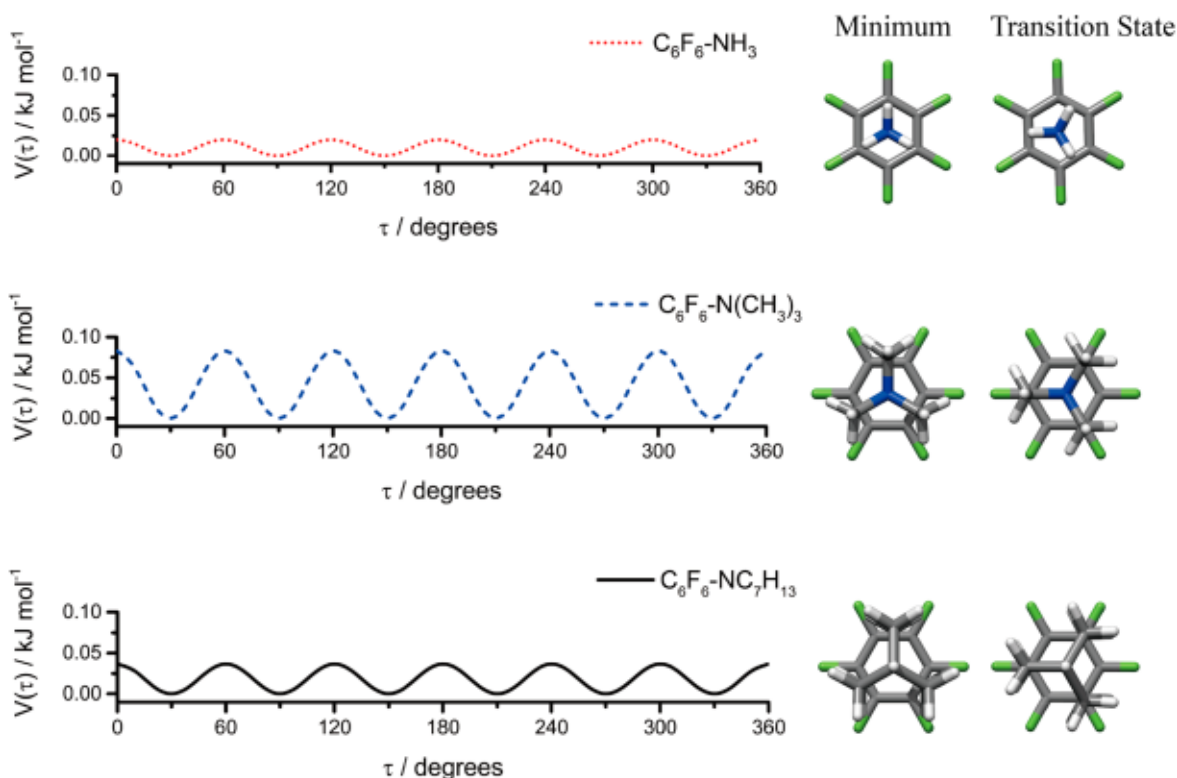
where

$$P_{ave} = \frac{1}{3}(P_{xx} + P_{yy} + P_{zz}) \quad (5)$$

Since, for a symmetric top  $P_{xx} = P_{yy}$ , eq 3 can now be written as

**Table 3.** Valence p-Orbital Population Anisotropy of the Complexes of  $C_6F_6-NH_3$ ,  $C_6F_6-N(CH_3)_3$ , and  $C_6F_6-NC_7H_{13}$

	Experimental		B3LYP-D4/def2-TZVP		
	$\chi$ (MHz)	$\Delta P_{zz}$	$\chi$ (MHz)	$\Delta P_{zz}^{\chi}$	$\Delta P_{zz}^{NBO}$
$C_6F_6-NH_3$	-3.17(2)	0.189(1)	-4.1408	0.245	0.319
$C_6F_6-N(CH_3)_3$	-5.43(41)	0.323(1)	-5.9087	0.352	0.367
$C_6F_6-NC_7H_{13}$	-5.15(2)	0.308(1)	-5.5509	0.330	0.378
$NH_3$	-4.08983(2) <sup>65</sup>	0.243442(1)	-4.2417	0.252	0.332
$N(CH_3)_3$	-5.500(2) <sup>66</sup>	0.327(1)	-5.9385	0.353	0.370
$NC_7H_{13}$	-5.192(4) <sup>67</sup>	0.309(2)	-5.5722	0.332	0.378



**Figure 3.** Potential energy functions for the internal rotation of  $NH_3$ ,  $N(CH_3)_3$ , and  $NC_7H_{13}$  relative to  $C_6F_6$  around their  $C_3$  axes.

$$\chi_{zz} = \frac{3}{2} \chi_0 \Delta P_{zz} \quad (6)$$

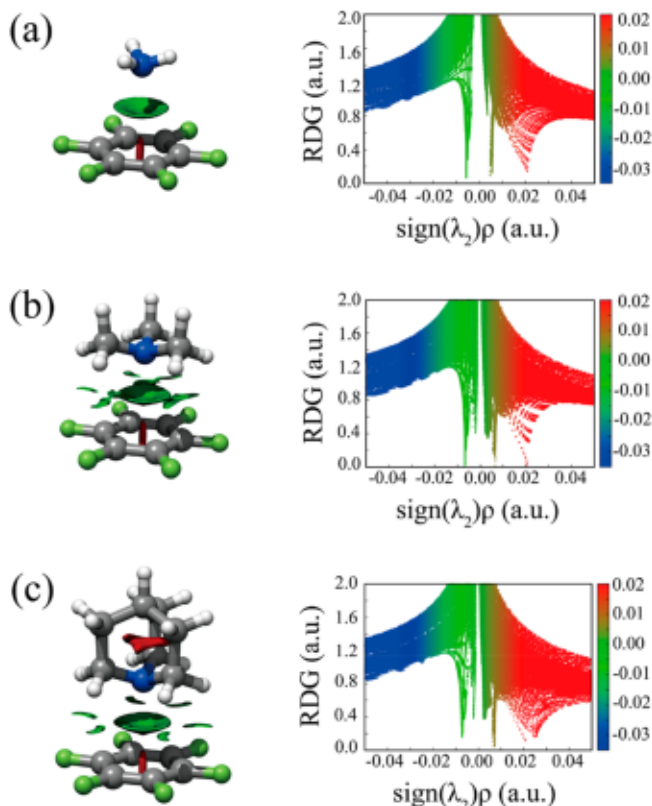
Therefore, the  $P$ -population anisotropy along the nitrogen lone pair direction can be directly estimated from the experimental nuclear quadrupole coupling constant. The  $\chi$  and  $\Delta P_{zz}$  values in the three complexes are compared to those of the monomers in Table 3, where also the theoretical values are listed. As regards the  $P$ -population anisotropy, two series of data are derived: one from the calculated  $\chi$  ( $\Delta P_{zz}^{\chi}$ ) and the other from the NBO<sup>62</sup> analysis of the p-orbitals population ( $\Delta P_{zz}^{NBO}$ ). As already discussed,<sup>57,63</sup> the positive value of  $\Delta P_{zz}$  is a direct measure of the strong electron density along the  $z$ -axis, while a negative value indicates a deficiency of electron density ( $\sigma$ -hole) which could lead to interaction with a nucleophilic group. The value of  $\Delta P_{zz}$  decreases going from the monomer to the complex for  $C_6F_6-NH_3$ . This could indicate an electron transfer from the N lone pair to the  $\pi$ -hole, which provides evidence for the formation of lp- $\pi$  interactions, but it could also be the effect of large-amplitude motions acting on the weakly bound ammonia molecule as shown in ref 64. It is not possible to disentangle these effects, but a close examination of the theoretical values and comparison to the experimental ones

can shed some light. Looking at Table 3 we can see that, for all monomers, the quadrupole coupling constants are reasonably reproduced. The differences between the calculated and experimental values are maintained for the complexes of trimethylamine and quinuclidine, while it is larger for the ammonia complex. The larger difference between theoretical and experimental values can be reasonably attributed to the large-amplitude motion's effects sizable for the ammonia complex but not for the other two due to the lower mass of ammonia. Nevertheless, we can also see that, for the ammonia complex, the theoretical values (free of the large-amplitude motion effects) indicate a larger change of the quadrupole coupling constants and  $\Delta P_{zz}$  in going from monomer to complex. Thus, the change in  $\Delta P_{zz}$  for the ammonia complex attributed in part to the large-amplitude motion effects and in part to the electronic transfer due to complexation. However, for the other two complexes, the values of  $\Delta P_{zz}$  remain nearly constant. This can be explained by the electron-donating ability of the alkyl substituents (vide infra), providing a buffer effect.

The potential energy as a function of the orientation of the ligands is calculated theoretically at the B3LYP-D4/def2-TZVP level. The potential energy function for the internal rotation of

$\text{NH}_3$ ,  $\text{N}(\text{CH}_3)_3$ , and  $\text{NC}_7\text{H}_{13}$  relative to  $\text{C}_6\text{F}_6$  around their  $C_3$  axes is shown in Figure 3. The low barriers being predicted (less than  $0.1 \text{ kJ mol}^{-1}$ ) and the observed symmetric top spectrum is consistent with both  $\text{N}(\text{CH}_3)_3$  and  $\text{NC}_7\text{H}_{13}$  rotating freely with respect to  $\text{C}_6\text{F}_6$ , as previously observed for  $\text{C}_6\text{F}_6\text{-H}_2\text{O}$ <sup>28</sup> and  $\text{C}_6\text{F}_6\text{-NH}_3$ .<sup>31</sup> The internal rotation barriers for  $\text{N}(\text{CH}_3)_3$  and  $\text{NC}_7\text{H}_{13}$  are slightly higher than that of  $\text{NH}_3$  with respect to  $\text{C}_6\text{F}_6$ . This result implies the formation of the intermolecular interaction of  $\text{CH}\cdots\text{F}$  in these two larger complexes. These weak  $\text{CH}\cdots\text{F}$  interactions need to be broken and reestablished during the torsion, thereby contributing to the barriers.

To obtain a better visualization of the intermolecular NCIs, Johnson's NCI method is applied.<sup>5</sup> The plots mapping the location and strength of NCIs are shown in Figure 4. The

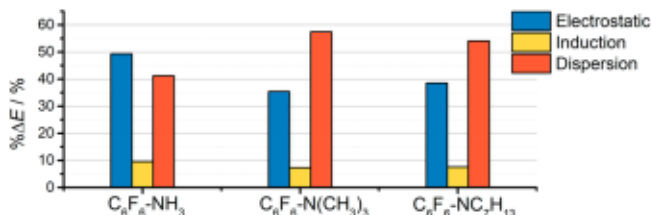


**Figure 4.** NCI plots from the electron densities ( $\rho$ ) for (a)  $\text{C}_6\text{F}_6\text{-NH}_3$ , (b)  $\text{C}_6\text{F}_6\text{-N}(\text{CH}_3)_3$ , and (c)  $\text{C}_6\text{F}_6\text{-NC}_7\text{H}_{13}$ , calculated at the B3LYP-D4/def2-TZVP level of theory. Left panel of NCI: reduced density gradient (RDG) isosurfaces colored according to the  $\text{sign}(\lambda_2)\rho$  ( $-0.04$ – $0.04 \text{ au}$ ). Color coding is blue-green (attractive interactions) and orange-red (repulsive interaction). Right panel of NCI: the RDG versus  $\text{sign}(\lambda_2)\rho$ . Positive  $\text{sign}(\lambda_2)\rho$  indicates repulsive interaction, and negative  $\text{sign}(\lambda_2)\rho$  indicates attractive interaction.

central green circle regions reveal the weak  $\text{lp}\text{-}\pi$  interactions, whereas the side green regions around the central region in  $\text{C}_6\text{F}_6\text{-N}(\text{CH}_3)_3$  and  $\text{C}_6\text{F}_6\text{-NC}_7\text{H}_{13}$  represent the weak  $\text{CH}\cdots\text{F}$  hydrogen bonds which are not present in  $\text{C}_6\text{F}_6\text{-NH}_3$ . The  $\text{CH}\cdots\text{F}$  hydrogen bonds become weaker in view of the area size of the NCI plots from  $\text{C}_6\text{F}_6\text{-N}(\text{CH}_3)_3$  to  $\text{C}_6\text{F}_6\text{-NC}_7\text{H}_{13}$ . This is consistent with the internal rotation potential function shown in Figure 3. The barrier of  $\text{C}_6\text{F}_6\text{-N}(\text{CH}_3)_3$  is higher than that of  $\text{C}_6\text{F}_6\text{-NC}_7\text{H}_{13}$ , which implies that the  $\text{CH}\cdots\text{F}$  hydrogen bonds are stronger in the former complex. This

indicates that the stronger overall intermolecular interaction in  $\text{C}_6\text{F}_6\text{-NC}_7\text{H}_{13}$  compared to  $\text{C}_6\text{F}_6\text{-N}(\text{CH}_3)_3$  could be attributed to the stronger  $\text{lp}\text{-}\pi$  interaction in the larger complex.

A quantitative understanding of the chemical nature of the NCIs has been achieved by energy decomposition analysis, using the symmetry-adapted perturbation theory (SAPT).<sup>68</sup> According to SAPT, the energy of the intermolecular interaction can be interpreted as the sum of different terms with defined physical meaning: electrostatic, induction, dispersion, and exchange-repulsion terms. The results summarized in Table S6 and Figure 5 show that the



**Figure 5.** SAPT energy decomposition for the complexes of  $\text{NH}_3$ ,  $\text{N}(\text{CH}_3)_3$ , and  $\text{NC}_7\text{H}_{13}$  with  $\text{C}_6\text{F}_6$ . The bar charts show electrostatic, induction, and dispersion energies as a percentage of total attractive interactions of each complex. See Table S6 for detailed values.

intermolecular interactions become stronger with increasing size of the alkyl substituent size. The relative energy scale allows for a general discussion of the driving forces of the different interactions. The electrostatic contribution, suggesting the  $\text{lp}\text{-}\pi$  interactions, is dominant in the intermolecular interactions of the  $\text{C}_6\text{F}_6\text{-NH}_3$  complex, whereas the London dispersion interactions dominate over the electrostatic interaction in the  $\text{C}_6\text{F}_6$ -alkylamines. This result indicates that the dispersion interactions are mainly responsible for the shorter  $r(\text{N}\cdots\text{C}_6\text{F}_6\text{CM})$  distances when going from  $\text{C}_6\text{F}_6\text{-NH}_3$  to  $\text{C}_6\text{F}_6$ -alkylamines. According to the NCI analysis, the increased dispersions are visualized as a few emerging weak dispersion-dominated  $\text{CH}\cdots\text{F}$  hydrogen bonds.<sup>40,69,70</sup> The dispersion interactions are also related to electron correlations in the whole molecules, and they become stronger as the size of the molecules and the number of electrons increase.<sup>71,72</sup> The higher proportion of electrostatic contribution and lower proportion of dispersion contribution in the intermolecular interactions of  $\text{C}_6\text{F}_6\text{-NC}_7\text{H}_{13}$  compared to that of  $\text{C}_6\text{F}_6\text{-N}(\text{CH}_3)_3$  indicates that the  $\text{lp}\text{-}\pi$  interaction is stronger in  $\text{C}_6\text{F}_6\text{-NC}_7\text{H}_{13}$  than that in  $\text{C}_6\text{F}_6\text{-N}(\text{CH}_3)_3$ , which coincides with the above analysis. This phenomenon invokes the role of the alkyl group as “electron buffer” that donates electrons to nitrogen as compensation for its consumption in the formation of  $\text{lp}\text{-}\pi$  interaction. The result is supported by a previous study where the alkylamines with larger alkyl groups tend to be better electron donors due to the electron-donating effect of alkyl groups.<sup>35</sup> In addition, it is consistent with the basicity of  $\text{NC}_7\text{H}_{13}$  ( $11.14 \text{ kcal mol}^{-1}$ )<sup>34</sup> being higher than that of  $\text{N}(\text{CH}_3)_3$  ( $8.82 \text{ kcal mol}^{-1}$ )<sup>33</sup> in aqueous solution. The electron-donating buffer effect of alkyl substituent also explains why the values  $\Delta P_{zz}$  of  $\text{C}_6\text{F}_6$ -alkylamines remain constant, instead of decreasing, when complexing with  $\text{C}_6\text{F}_6$  (Table 3). It is worth noting that the NCI and SAPT results should generally be taken with care, especially in studies where no consistency check with electron distribution sensitive observ-

ables like nuclear quadrupole coupling constant is available, as they might be less reliable as assumed.

In summary, the pure rotational spectra of the  $C_6F_6-N(CH_3)_3$  and  $C_6F_6-NC_7H_{13}$  complexes have been measured in the 2–18 GHz range. The rotational constants, the centrifugal distortion constants, and nuclear quadrupole coupling constants for both complexes are reported and compared to those of  $C_6F_6-NH_3$ . These three complexes exhibit  $C_{3v}$  symmetry and undergo internal rotation along their  $C_3$  axes. As the size of the alkyl substituents increases, the  $N\cdots\pi$ -center distance decreases and the intermolecular interaction increases. This phenomenon is attributed to the interplay between dispersion interaction and electrostatic interaction as revealed by the quantitative energy decomposition analysis. The increased intermolecular interaction in going from  $C_6F_6-NH_3$  to  $C_6F_6$ -alkylamines is due to the increased dispersion contribution, while the increased intermolecular interaction from  $C_6F_6-N(CH_3)_3$  to  $C_6F_6-NC_7H_{13}$  is attributed to electrostatic interaction. The values of the  $P$ -population anisotropy along the nitrogen lone pair direction ( $\Delta P_{zz}$ ) remain constant during complexing with  $C_6F_6$  for both  $C_6F_6-N(CH_3)_3$  and  $C_6F_6-NC_7H_{13}$ , while  $\Delta P_{zz}$  decreases going from  $NH_3$  to the complexes of  $C_6F_6-NH_3$ . This result indicates that the alkyl groups act as an “electron buffer” when alkylamines complex with  $C_6F_6$ , and the alkyl groups can donate electrons to nitrogen as compensation for its compulsion in the formation of lp- $\pi$  interaction.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcclett.3c00882>.

Experimental and theoretical details; The diagram of the CP-FTMW spectrometer at Fudan University; The structural informations of the complexes of  $C_6F_6-NH_3$ ,  $C_6F_6-N(CH_3)_3$ , and  $C_6F_6-NC_7H_{13}$ ; Measured rotational transition frequencies; SAPT analysis (PDF)

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## Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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