[\textit{NH \ldots N}^+] \textit{Hydrogen Bonds in Crystalline Salts of Monoaza- and Diaza-bicyclo[2.2.2]octane}

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IR and Raman spectra and phase transitions have been studied on various salts of azabicyclo[2.2.2]octane (ABCO) and 1,4-diaza-bicyclo[2.2.2]octane (DABCO) which forms with simple strong acids adducts of 2:1, 1:1 and 1:2 composition. Only 2:1 DABCO adducts form homoconjugated cations containing \([\text{NH} \cdot \cdot \cdot \text{H}]^+\) hydrogen bonds close to symmetrical ones, showing broad absorption in the low frequency region and strong temperature effect. The Evans holes observed in this case can be ascribed to a coupling of protonic vibrations with skeletal \(\delta_8 (N-C_3)\) and \(\delta_{as} (N-C_3)\) modes.

1,4-Diaza-bicyclo[2.2.2]octane (DABCO) and azabicyclo[2.2.2]octane (ABCO) are potentially interesting components of homoconjugated cations. This is due to the relatively rigid structure of the molecules and baring nitrogen basic centers and also to a fairly high symmetry and globular structure. Bicenter amine — DABCO creates additional possibilities of interaction forming with acids AH three types of adducts, namely DABCO \cdot HA, (DABCO)$_2$ \cdot HA and DABCO \cdot (HA)$_2$. In some particular cases of 1:1 adducts with simple strong acids like HClO$_4$ and HBF$_4$ polycations (I) are formed in the crystalline lattice,

\[ \text{I} \]

while in the case of 2:1 salts simple homoconjugated bocations (II) are formed

\[ \text{II} \]

In polycations (I) particularly long hydrogen bonds N—H \ldots N were found\textsuperscript{1} what is also reflected in the position of stretching vibration band \(v_{\text{NH} \cdot \cdot \cdot \text{H}^{\text{as}}}\); this

\textsuperscript{1} Festschrift of Professor Dušan Hadži.
band for bication (II) is located at much lower frequencies typical for the majority of homoconjugated bocations. Moreover, it is well known that 1 : 1 salts of DABCO do not show the continuous broad absorption in the infrared and anomalous temperature effect in the low frequency part of broad absorption. These effects, as has been established in this paper, are particularly evident only in the case of bication (II). The investigation of these effects and appearance of the Evans holes seemed to be of particular interest. We suggested that the source of the Evans holes is the coupling of protonic vibrations with internal low frequency modes of the base molecules which give rise to the modulation of the bridge geometry and particularly to its length¹.

**EXPERIMENTAL**

The perchlorate and the tetrafluoroborate of DABCO have been crystallized from stoichiometric solutions in methanol (melting point at \( \sim 563 \) and \( \sim 547 \) K respectively is accompanied by decomposition and sublimation). The hemiperchlorate and the hemitetrafluoroborate have been obtained from 1 : 1 salts by crystallization from solution in acetonitrile at an excess of the base. The 2 : 1 salts undergo above \( 420 \) K a decomposition into 1 : 1 salts and free base.

IR absorption spectra of the salts in Nujol and hexachlorobutadiene suspensions have been recorded in Perkin Elmer 180 and 621 Spectrophotometers using CSJ, KRS-5 or polyethylene plates. The low temperature spectra have been measured using a vacuum cryostat. Raman spectra of polycrystalline substances have been recorded on a Coderg PH 01 spectrometer supplied with He–Ne laser excitation source (6328 Å). The observations of phase transitions have been performed by using OD-102 derivatograph.

**RESULTS AND DISCUSSION**

\( v_{\text{NH}...N} \) stretching vibration band. As can be seen from the survey spectra shown in Figure 1 both the position and the width of the band indicate that the hydrogen bond in (II) is much stronger than that in (I). The length of the hydrogen bond in (I) equals to 2.84 Å. Unfortunately X-ray diffraction studies for crystals of the (II) type did not succeed because of instability. If one takes into account the data collected so far on the correlation between \( v_{\text{NH}...H} \) and \( R_{\text{N}...N} \) than we can estimate the \( R_{\text{N}...N} \) value for cation (II) as equal to about 2.65 Å. This value is only a little greater than those for symmetrical NHN bridges which have been established in quinuclidone-3 hemiperchlorate 2.63 Å⁶ and \( \text{H}_3\text{Co(CN)}_6 \) 2.582 Å⁵. It seems that the situation in our case is similar to that in \( \text{Py}_2\text{H}^+ \)⁷ and \( (4\text{-NH}_2\text{Py})_2\text{H}^+ \)⁸, where the asymmetrical NHN bridges exist although the proton is markedly shifted to the bridge center.

The isotopic effect is typical for hydrogen bonded systems i.e. the \( v_{\text{NHN}}/v_{\text{NDN}} \) ratio for (I) equals to 1.27 and for (II) \( \sim 1.2 \) (the values are close to those reported in⁹). Isotopic ratios should be considered with some caution because the position of the \( v_{\text{NDN}} \) bands can be determined only with great uncertainty particularly for the (II) salts; their band is shifted to the fingerprint region.

Internal vibration of DABCO. In the spectra of DABCO salts one finds the bands characteristic for free DABCO with minor frequency shifts and — in a few cases — with splittings. The symmetry change for 1 : 1 and 2 : 1 adducts \((D_{sh} \rightarrow C_{nv})\) is clearly evident in the activation of the bending vibrations \( \delta_{\text{N}--\text{C}} \)⁹ which for free DABCO are observed only in the Raman spectrum. As we have shown in this paper, only this mode is strongly coupled with
protonic vibrations. The manifestation of $\delta_s(N-C_3)$ vibrations in various salts is presented in Table I together with other skeletal modes.

As expected, some changes in the intensity of most part of the bands and slight shifts of their position as compared with the base itself are observed. Distinguished deviations take place in the skeletal vibrations picture for the 2:1 salt in which bicitons (II) are present. For two vibrations $\delta_s(N-C_3)$ and $\delta_{as}(N-C_3)$ at about 415 and 600 cm$^{-1}$ (marked in the Table by means of arrows) the Evans holes appear on the envelope of broad protonic absorption. It seems that only these two modes couple with protonic vibrations. In the case of other salts neither broad low frequency absorption nor anomalous temperature effect occur and usual bands of skeletal vibrations are observed.

Continuous absorption and temperature effect. It is seen in Figure 1 that the continuous absorption for (DABCO)$_2$H$^+$ covers the infrared region down to 200 cm$^{-1}$ with a particularly intense Evans hole at about 600 cm$^{-1}$ where for other salts normal absorption band appears. In the case of perchlorates the picture is somewhat obscured because of overlapping with the ClO$_4^-$ absorption band.

A decrease of temperature leads to a drastic rise of absorption intensity below 1000 cm$^{-1}$, maintaining the deep Evans hole. The extension of this effect is illustrated in Figure 2. Simultaneously it is worth emphasizing that parallely with the decrease of temperature down to 90 K continuous shift of the $\nu_{NNH}$ stretching vibration band takes place as much as about 150–200 cm$^{-1}$ to lower frequency. It means that remarkable lattice contraction and shortening of the N...N bridge does occur.

It seems very interesting that in the case of ABCO hemiperclorate, which is a very close analogue of DABCO salt, neither the continuous absorption nor the anomalous temperature effect in low frequency range appears. The reason for such difference arises most probably from the fact that the hydrogen bond in (ABCO)$_2$H$^+$ is weaker and this is reflected in the frequency of the $\nu_{NH-N}$ band (2200 cm$^{-1}$ as compared with 1900 cm$^{-1}$ for (DABCO)$_2$H$^+$).

![Figure 1. IR spectra of DABCO hemiperclorate (solid line) and DABCO tetrafluoroborot (dotted line) in Nujol.](image-url)
TABLE I

Skeletal Vibrations of DABCO and Its Salts

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Description</th>
<th>DABCO&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DABCO·HBF&lt;sub&gt;4&lt;/sub&gt;</th>
<th>DABCO·1/2 HBF&lt;sub&gt;4&lt;/sub&gt;</th>
<th>DABCO·2HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IR</td>
<td>R</td>
<td>IR</td>
<td>R</td>
<td>IR</td>
</tr>
<tr>
<td>E''</td>
<td>332 w</td>
<td>—</td>
<td>—</td>
<td>325 s</td>
<td>330 s</td>
</tr>
<tr>
<td>E'</td>
<td>425 vw</td>
<td>423 w</td>
<td>408, 415 w</td>
<td>415 w</td>
<td>414&lt;sub&gt;v&lt;/sub&gt; w</td>
</tr>
<tr>
<td>E''</td>
<td>579 w</td>
<td>—</td>
<td>—</td>
<td>565 w</td>
<td>—</td>
</tr>
<tr>
<td>A'&lt;sub&gt;1&lt;/sub&gt;</td>
<td>596 w</td>
<td>—</td>
<td>613 vs</td>
<td>610 w</td>
<td>600&lt;sub&gt;v&lt;/sub&gt; vs</td>
</tr>
<tr>
<td>E'</td>
<td>830 m</td>
<td>805 m</td>
<td>804 s</td>
<td>803 vs</td>
<td>802 s</td>
</tr>
<tr>
<td>A'&lt;sub&gt;2&lt;/sub&gt;</td>
<td>897 m</td>
<td>897 w</td>
<td>900 mw</td>
<td>900 w</td>
<td>900 w</td>
</tr>
<tr>
<td>A'&lt;sub&gt;1&lt;/sub&gt;</td>
<td>961 m</td>
<td>—</td>
<td>?</td>
<td>978 w</td>
<td>980 m</td>
</tr>
<tr>
<td>E'</td>
<td>986 m</td>
<td>—</td>
<td>(1000)</td>
<td>1000 w</td>
<td>(1010)</td>
</tr>
<tr>
<td>E'</td>
<td>1057 vs</td>
<td>1061 mw</td>
<td>?</td>
<td>1055 w</td>
<td>(1055)</td>
</tr>
</tbody>
</table>

<sup>a</sup>DABCO.
The strong temperature effect has been interpreted assuming that the broad low frequency absorption is due to the 'tunneling' transition for the case with double minimum potential of low barrier. We have shown that absorption intensity and its frequency distribution depends strongly on the bridge length and on the population of stretching bridge vibrational levels. A decrease of temperature leads to both the shortening of the bridge and an increase of population of low energy levels and, as a consequence, to the change of the potential energy curve for the proton motion. Unfortunately, there is a lack of direct evidence based on neutron diffraction studies. The above hypothesis is only supported by changes of the position of $\nu_{NH}$ stretching vibration band.

The above interpretation of broad absorption in the low frequency region and its temperature sensitivity is close to that proposed by Zundel et al. They pay also special attention to the double minimum potential function for the proton motion. A symmetrization of the bridge should lead, according to Zundel's concept to a strong increase of the polarizability and owing to the interaction with surrounding hydrogen bonds and fluctuating electric field to the diffusion of energy levels.

The length of the hydrogen bond and the shape of the potential energy curve for the proton motion appeared to be extremely sensitive to the...
lattice effects. The difference between the polycation (I) and simple bication (II) is easy to understand keeping in mind a strong polarization effect in polycation. It is more difficult to explain the striking difference between (DABCO)$_2$H$^+$ and (ABCO)$_2$H$^+$. From the unpublished results of Roziere it follows that the quinuclidone-3 forms homoconjugated cations with symmetrical location of proton in spite of the fact that the quinuclidone-3 molecule possesses lower symmetry.

Considering the temperature effect on IR-spectra of salt (II) it is necessary to take into account a possible influence on IR spectrum of the phase transitions connected with motions of DABCO molecules as well as in the case of ABCO. Pure crystalline DABCO undergoes two transformations at 175 and 351 K. The low temperature one is attributed to the freezing of rotational motion around 1–4 axis, whereas the high temperature transition in connected with releasing more complicated rotational reorientations close to free rotation in plastic phases.

In the case of 2 : 1 and 1 : 1 salts of DABCO analogous low temperature transition takes place, which for (DABCO)$_2$HClO$_4$ adduct undergoes at about 100 K i.e. below the transition for amine itself. Therefore, spectral changes under cooling are not due to the phase transition; an enhancement of intensity in the low frequency range follows continuously and reversibly.

*Bridge vibrations.* In the far infrared region a broad band at about 100 cm$^{-1}$ is observed which can be ascribed to the bridge vibrations. Two maxima bot for (I) and (II) salts can be distinguished but it is impossible to ascribe them to specified modes. According to the expectations the intensity for the (I) salt is much higher than for the (II) salt, whereas the frequency for (II) is about 10–20 cm$^{-1}$ higher than for (I) (a stronger and a more symmetrical hydrogen bridge).

As we have already mentioned, for adduct of (II) type the beginning of continuous absorption in the far infrared region is observed which — as can be seen in Figure 3 — does not appear for polycation (I).

![Figure 3. Far IR spectra of DABCO perchlorate (1) and DABCO hemiperchlorate (2) in Nujol.](image-url)
N—H·· ·N HYDROGEN BONDS

REFERENCES

6. J. Rozière, private information.

IZVLEČEK

Vodikove vezi (NH·· ·N) v kristalnih soli mono-aza in diaza-biciklo [2,2,2]oktana

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1,4-diazabiciklo[2,2,2]oktan (DABCO) in azabiciklo [2,2,2]oktan (AMCO) so potencialno zanimive komponente homokonjugiranih kationov, zaradi relativno toge strukture in precej visoke simetrije. Bicenterski amin DABCO lahko tvori s kislinitmi tri vrste aduktov: DABCO·HA, (DABCO)2·HA in DABCO·(HA)2. V nekaterih posebnih primerih aduktov 1:1 se tvorijo polikationi (I.), medtem ko v primeru soli 2:1 najdemo preproste homokonjugirane bikatione (II.). Polikationi vsebujejo precej dolge vodikove vezi NH·· ·N, katerih razdalja znaša 2.84 Å, medtem ko je vodikova veža bikationa IL znatno krajša in ocenjena na 2,65 Å.

Ustreznii infrardeči spektri slednjega kažejo široki absorpcijski trak v nizkofrekvenčnem delu spektra, zelo močno temperaturno odvisnost frekvence in intenzivnosti tega traku. Dve Evansovi luknji v tem području pri 415 in 600 cm⁻¹ pripišujemo interakcijam dveh skeletnih nihanj, νs(N—Cα) in νas(N—Cα) s širokim nivojem valenčnega nihanja NH skupine. V daljnjem infrardečem področju opazimo širok trak blizu 100 cm⁻¹, ki ustreza nihanju vodikove vezi.