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[NH . . . N]$^+$ Hydrogen Bonds in Crystalline Salts of Monoaza- and Diaza-bicyclo[2.2.2]octane

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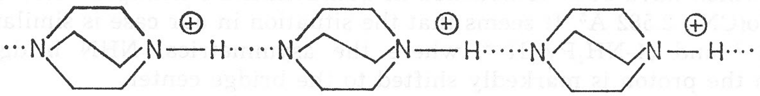
IR and Raman spectra and phase transitions have been studied on various salts of azabicyclo[2.2.2]octane (ABCO) and 1,4-diazabicyclo[2.2.2]octane (DABCO) which forms with simple strong acids adducts of 2 : 1, 1 : 1 and 1 : 2 composition. Only 2 : 1 DABCO adducts form homoconjugated cations containing [NH···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 δ_s (N—C$_3$) and δ_{as} (N—C$_3$) modes.

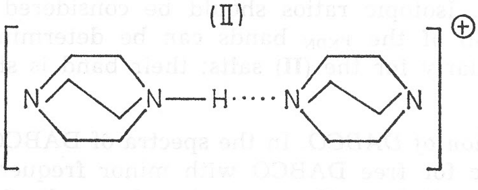
1,4-Diazabicyclo[2.2.2]octane (DABCO) and azabicyclo[2.2.2]octane (ABCO) are potentially interesting components of homoconjugated cations. This is due to the relatively rigid structure of the molecules and baring nitrogen basic centers and also to a fairly high symmetry and globular structure. Bicenter amine — DABCO creates additional possibilities of interaction forming with acids AH three types of adducts, namely DABCO · HA, (DABCO)$_2$ · HA and DABCO · (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,

(I)



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

(II)



In polycations (I) particularly long hydrogen bonds N—H . . . N were found[1] what is also reflected in the position of stretching vibration band $\nu_{NH..H}$[2,3]; this

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* Festschrift of Professor Dušan Hadži.

band for bication (**II**) is located at much lower frequencies typical for the majority of homoconjugated bications. 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 length[4].

EXPERIMENTAL

The perchlorate and the tetrafluoroborate of DABCO have been crystallized from stoichiometric solutions in methanol (melting point at ~ 563 and ~ 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

$\nu_{NH\ldots N}$ *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 $\nu_{NH\ldots H}$ and $R_{N\ldots N}$ than we can estimate the $R_{N\ldots N}$ 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 Å[6] and $H_3Co(CN)_6$ 2.582 Å[5]. It seems that the situation in our case is similar to that in Py_2H^+[7] and $(4\text{-}NH_2Py)_2H^+$[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 ν_{NHN}/ν_{NDN} ratio for (**I**) equals to 1.27 and for (**II**) ~ 1.2 (the values are close to those reported in[2]). Isotopic ratios should be considered with some caution because the position of the ν_{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 ($D_{3h} \rightarrow C_{3v}$) is clearly evident in the activation of the bending vibrations $\delta_s(N\text{—}C_3)$[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 $\delta_s(\mathrm{N{-}C_3})$ 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 bications (**II**) are present. For two vibrations $\delta_s\,(\mathrm{N{-}C_3})$ and $\delta_{as}\,(\mathrm{N{-}C_3})$ at about 415 and 600 $\mathrm{cm^{-1}}$ (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 $\mathrm{(DABCO)_2H^+}$ covers the infrared region down to 200 $\mathrm{cm^{-1}}$ with a particularly intense Evans hole at about 600 $\mathrm{cm^{-1}}$ where for other salts normal absorption band appears. In the case of perchlorates the picture is somewhat obscured because of overlapping with the $\mathrm{ClO_4^-}$ absorption band.

A decrease of temperature leads to a drastic rise of absorption intensity below 1000 $\mathrm{cm^{-1}}$, maintaining the deep Evans hole. The extention 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 ν_{NHN} stretching vibration band takes place as much as about 150—200 $\mathrm{cm^{-1}}$ 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 hemiperchlorate, 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 $\mathrm{(ABCO)_2H^+}$ is weaker and this is reflected in the frequency of the $\nu_{\mathrm{NH..N}}$ band (2200 $\mathrm{cm^{-1}}$ as compared with 1900 $\mathrm{cm^{-1}}$ for $\mathrm{(DABCO)_2H^+}$).

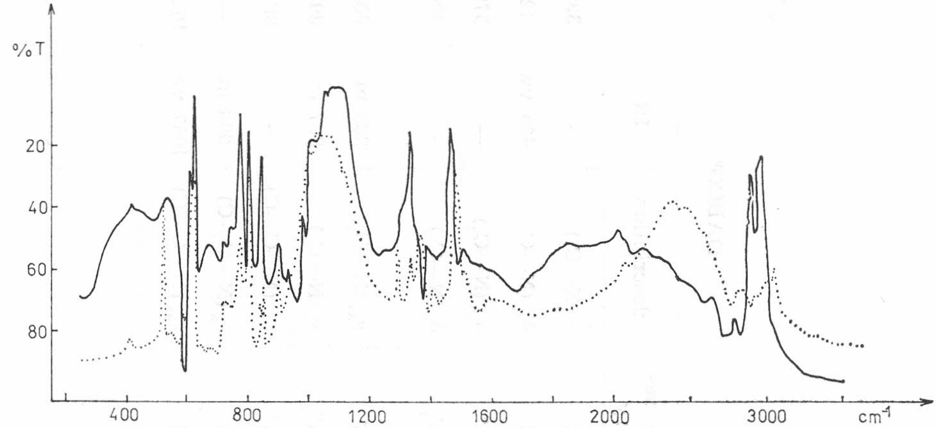

Figure 1. IR spectra of DABCO hemiperchlorate (solid line) and DABCO tetrafluoroborate (dotted line) in Nujol.

TABLE I

Skeletal Vibrations of DABCO and Its Salts

DABCO[9]				DABCO · HBF_4		DABCO 1/2 HBF_4		DABCO · 2HCl	
Symmetry	description	IR	R	IR	R	IR	R	IR	R
E''	ϱ (N—C_3)	—	332 w	—	325 s	—	330 s	314, 318 m	320 m
E'	δ_{as} (N—C_3)	425 vw	423 w	408, 415 w	415 w	414↓ w	420 w	406 m	410 m
E''	δ_{as} (N—C_3)	—	579 w	—	565 w	—	555, 573 w	556 wm	556 w
A'_1	δ_s (N—C_3)	—	596 w	613 vs	610 w	600↓ vs 612 w	?	604 w	604 s
E'	ν_{as} (N—C_3)	830 m	805 m	804 s	803 vs	802 s	806 m	804 w	805 vs
A''_2	ν_s (N—C_3)	897 m	897 w	900 mw	900 w	900 w	900 w		
A'_1	ν_{as} (N—C—C)	—	961 m	?	978 w	980 m	983 m	976 s	983 m
E'	ν_s (N—C—C)	986 m	—	(1000)	1000 w	(1010)		992 m	
E'	ν_{as} (N—C—C)	1057 vs	1061 mw	?	1055 w	(1055)	1060 m	1054 vs	1058 m

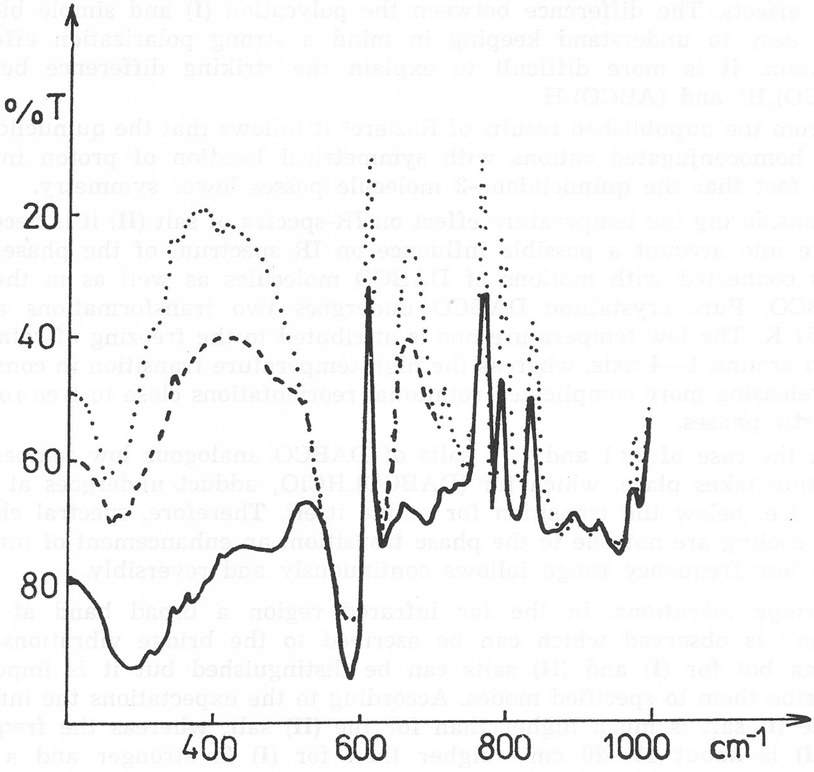

Figure 2. Temperature effect on IR spectrum of DABCO hemitetrafluoroborate in Nujol: solid line — room temperature, dotted — 90 K, dashed — 170 K.

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 ν_{NHN} 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.[10]. 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 $(DABCO)_2H^+$ and $(ABCO)_2H^+$.

From the unpublished results of Roziere[6] it follows that the quinuclidone-3 forms homoconjugated cations with symmetrical location of proton in spite of the fact that the quinuclidone-3 molecule posses 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 $(DABCO)_2HClO_4$ 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**).

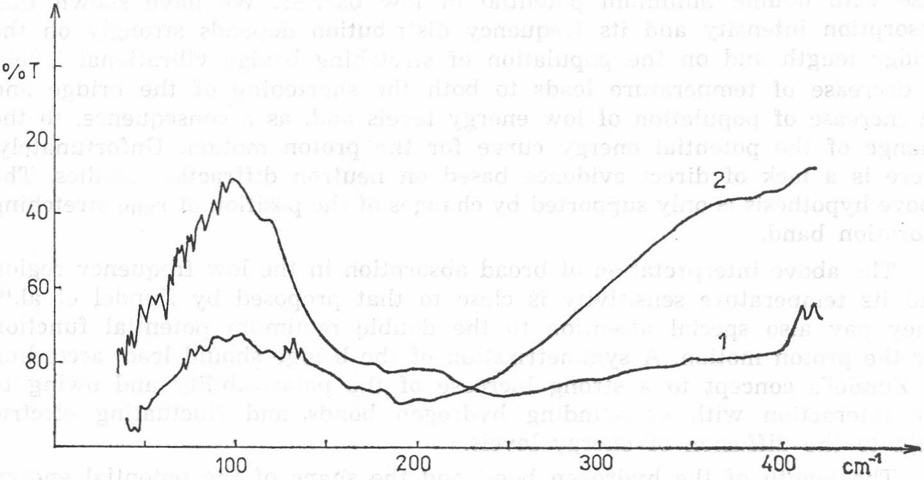

Figure 3. Far IR spectra of DABCO perchlorate (1) and DABCO hemiperchlorate (2) in Nujol.

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IZVLEČEK

Vodikove vezi $(NH\cdots N)^+$ v kristalih soli mono-aza in diaza-biciklo [2,2,2]oktana

Eugeniusz Grech, Zbigniew Malarski in Lucjan Sobczyk

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 kislinami tri vrste aduktov: DABCO·HA, $(DABCO)_2\cdot HA$ in $DABCO\cdot (HA)_2$. 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 vez bikationa II. znatno krajša in ocenjena na 2,65 Å.

Ustrezni 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 področju pri 415 in 600 cm^{-1} pripisujemo interakcijam dveh skeletnih nihanj, $\nu_s(N—C_3)$ in $\nu_{as}(N—C_3)$ s širokim nivojem valenčnega nihanja NH skupine. V daljnem infrardečem področju opazimo širok trak blizu 100 cm^{-1}, ki ustreza nihanju vodikove vezi.