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Vibrational Spectrum of Trisdimethylaminocyclopropenium Perchlorate

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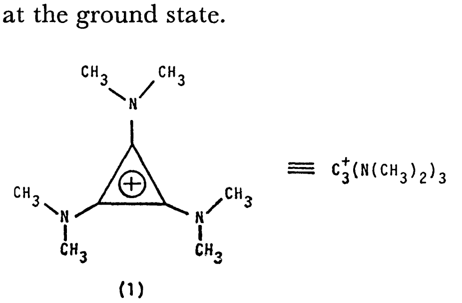
Infrared spectrum in the region 4000—100 cm^{-1} and Raman spectrum of trisdimethylaminocyclopropenium perchlorate (1) have been measured. Band assignments have been made on the basis of normal coordinate analysis and deuteration of the methyl groups. Remarkable stabilization of cyclopropenium ion due to the peripheral amino groups is attributed to a marked delocalization of the positive charge of the ring on the amino groups through conjugation. Peculiar electronic structure of trisaminocyclopropenium ion is explained in terms of its vibrational spectrum.

Cyclopropenium cations have received much attention in both the field of organic chemistry and molecular spectroscopies, mainly because of the fact that the smallest non-benzenoid aromatic cation (2π electron system) possesses high strain energy. The infrared spectrum of this system is usually discussed on the characteristic bands assigned to the skeletal vibrations of the three membered ring (C_3^+ core). The normal coordinate analysis of parent,[11] trimethyl-[11] and trichloro-cyclopropenium cations[1,11] was carried out using the Urey-Bradley force field. The calculation by the GVFF method was also reported for trichloro- and triphenyl-cyclopropenium cations in the simplified model.[2] However, no vibrational spectra of the cyclopropenium ion substituted with the strongly electron donating group (X) have been found so far. Such a tri-X-substituted cyclopropenium ion is considered to offer a good model for the investigation of physical and chemical properties of the strongly perturbed cyclopropenium ion.

Recently we have succeeded in the synthesis of triaminocyclopropenium ion[3] which is very stable (even in hot water) in contrast to the cyclopropenium ions reported so far. Thus the unusual physico-chemical properties of triaminocyclopropenium ion are expected to reflect on its vibrational spectrum. The present paper deals with the vibrational spectra of tris(dimethylamino)cyclopropenium ion(1) and its deutero analog in order to elucidate its structural feature at the ground state.



(1)

Experimental

1,2,3-Trisdimethylaminocyclopropenium perchlorate (1) was obtained by the treatment of tetrachlorocyclopropene with dimethylamine in methylene chloride.[3] Deuteration was performed with dimethylamine hydrochloride-d_6 (99%, E. Merck Co.) as a starting material.

The infrared spectra between 4000 and 300 cm^{-1} were recorded on a Perkin-Elmer Model 521 spectrophotometer and the far-infrared spectra on a Perkin-Elmer-Hitachi FIS-3 far-infrared photometer. The KBr-pellet technique was used for the former and the Nujol mull technique with a polyethylene window for the latter. Raman spectrum in the solid state was recorded on a JASCO R-1100 spectrophotometer with He–Ne laser (6328 Å).

Normal Coordinate Analysis

Figure 1 illustrates the molecular model and the internal coordinates used for normal coordinate analysis. According to a recent crystallographic study[4] of (1), the molecular symmetry can be approximated to D_{3h}. Out-of-plane deviations of six methyl groups are found to be very small. In order to simplify the calculation, each of the six methyl groups is treated as a single atom having a mass of 15.035. The G-matrix elements were evaluated by using the structure parameters listed in Table 1. These values were slightly changed from those of the original X-ray study in order to adjust the molecular dimension to D_{3h} symmetry.[6] Thus in this model, thirty normal vibrations, 30 ($12 \times 3-6$), are grouped into $4A_1'+3A_2'+$

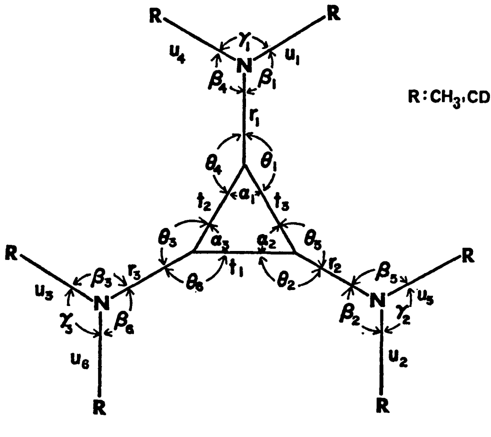


Fig. 1. Internal coordinates for the in-plane vibrations of trisdimethylaminocyclopropenium ion.

TABLE 1. MOLECULAR DIMENSIONS

Bond length (Å)	Bond angle
d(N-R) = 1.457 (1.457)	∠C-N-R = 120° (119.5°)
d(C-N) = 1.332 (1.333)	∠R-N-R = 120° (119.0°)
d(C-C) = 1.362 (1.363)	∠N-C-C = 150° (150.0°)
	∠C-C-C = 60° (60.0°)

Values in brackets indicate the average value from X-ray analysis.[4]

TABLE 2. SYMMETRY COORDINATES FOR IN-PLANE VIBRATIONS

	Symmetry coordinate	Vibration mode[a]
A_1'	$S_1=(\Delta t_1+\Delta t_2+\Delta t_3)/\sqrt{3}$	ν(C-C)
	$S_2=(\Delta r_1+\Delta r_2+\Delta r_3)/\sqrt{3}$	$\nu(C_3^+\text{-R})$
	$S_3=(\Delta s_1+\Delta s_2+\Delta s_3+\Delta s_4+\Delta s_5+\Delta s_6)/\sqrt{6}$	ν(N-R)
	$S_4=(2\Delta\gamma_1-\Delta\theta_1-\Delta\theta_4+2\Delta\gamma_2-\theta_2-\Delta_5+2\Delta\gamma_3-\Delta\theta_3-\Delta\theta_6)/3\sqrt{2}$	δ(R-N-R)
E′	$S_5=(2\Delta t_1-\Delta t_2-\Delta t_3)/\sqrt{6}$	ν(C-C)
	$S_6=(2\Delta r_1-\Delta r_2-\Delta r_3)/\sqrt{6}$	ν(C-N)
	$S_7=(2\Delta s_1+2\Delta s_4-\Delta s_3-\Delta s_6-\Delta s_2-\Delta s_5)/\sqrt{12}$	ν(N-R)
	$S_8=(\Delta s_2+\Delta s_6-\Delta s_3-\Delta s_5)/2$	ν(N-R)
	$S_9=(4\Delta r_1-2\Delta\theta_1-2\Delta\theta_4-2\Delta\gamma_2+\Delta\theta_2+\Delta\theta_5-2\Delta\gamma_3+\Delta\theta_3+\Delta\theta_6)/(6)$	δ(R-N-R)
	$S_{10}=(\Delta\theta_2+\Delta\theta_6-\Delta\theta_3-\Delta\theta_5)/(2)$	$\delta(C_3^+\text{-N-R})$
	$S_{11}=(4\Delta\alpha_1-2\Delta\beta_1-2\Delta\beta_4-2\Delta\alpha_2+\Delta\beta_2+\Delta\beta_5-2\Delta\alpha_3+\Delta\beta_3+\Delta\beta_6)/(6)$	ring def.
	$S_{12}=(\Delta\beta_2-\Delta\beta_5-\Delta\beta_3+\Delta\beta_6)/2$	δ(C-C-N)

a) Symbols ν and δ denote stretching and in-plane bending vibrations, respectively.

$7E'+1A_2''+3E''$). There are sixteen infrared active modes; 7E′ (in-plane) and $2A_2''$ (out-of-plane), and twenty four Raman active modes; 7E′ (in-plane), $4A_1'$ (in-plane) and 3E″ (out-of-plane). We have calculated eleven in-plane vibrations (7E′ and $4A_1'$) by means of Wilson's GF matrix method. The twelve symmetry coordinates used in the calculation are given in Table 2.

The F-matrix elements are expressed by the simple Urey-Bradley force field. In the first calculation, the stretching force constants K(C–C), K(C–N), and K-(N–CH_3) were estimated from those of trichlorocyclopropenium ion,[1] guanidium salt,[7] and alkyl urea,[8] respectively. The bending and repulsive forec constants were transferred from those of the amide compounds.[9]

The computational procedures were carried out by using the FACOM in Kyoto University. The final set of force constants were obtained by referring to the Jacobian matrix elements followed by further refinement using the least squares method (Table 3). Calculated frequencies are compared with those observed for (1) and (1)-d_{18} (Table 4). We see that agreement is quite satisfactory in spite of a single mass approximation for the methyl group. For the band assignments, the potential energy distribution was calculated for each normal vibration in terms of the symmetry coordinates are shown in the last column of Table 4.

TABLE 3. UREY-BRADLEY FORCE CONSTANTS OF TRISDIMETHYLAMINOCYCLOPROPENIUM ION (in mdyn/Å)

K(C-C)	6.622
K(C-N)	5.741
K(N-R)	4.270
H(C-C-C)	−1.014
H(C-C-N)	0.615
$H(C_3^+\text{-N-R})$	0.203
H(R-N-R)	0.353
F(C----N)	0.659
F(C----R)	0.430
F(R----R)	0.039

TABLE 4. COMPARISON OF OBSERVED AND CALCULATED FREQUENCIES

		Obsd	Calcd	PED
		(I)		
(A_1')	ν_1	1985	1985	$S_1(80)$, $S_2(38)$
	ν_2	1135	1140	$S_1(11)$, $S_2(30)$, $S_3(45)$, $S_4(14)$
	ν_3	614	607	$S_2(21)$, $S_3(55)$, $S_4(14)$
	ν_4	324	310	$S_2(15)$, $S_4(74)$
(E′)	ν_5	1553	1545	$S_5(42)$, $S_6(70)$, $S_{11}(11)$
	ν_6	1280	1278	$S_6(12)$, $S_8(52)$, $S_{10}(13)$, $S_{12}(20)$
	ν_7	1120	1097	$S_5(42)$, $S_7(18)$, $S_8(37)$, $S_{11}(11)$
	ν_8	790	780	$S_6(12)$, $S_7(60)$
	ν_9	460	463	$S_5(10)$, $S_7(13)$, $S_9(55)$, $S_{10}(13)$
	ν_{10}	316	319	$S_5(22)$, $S_9(35)$, $S_{10}(30)$
	ν_{11}	130	131	$S_{10}(40)$, $S_{12}(50)$
		(II)-d_{18}		
(A_1')	ν_1	—	1985	$S_1(80)$, $S_2(38)$
	ν_2	—	1124	$S_1(12)$, $S_2(32)$, $S_3(41)$, $S_4(14)$
	ν_3	—	561	$S_2(19)$, $S_3(60)$, $S_4(12)$
	ν_4	—	283	$S_2(14)$, $S_4(74)$
(E′)	ν_5	1534	1544	$S_5(42)$, $S_6(70)$, $S_{11}(11)$
	ν_6	1252	1262	$S_6(13)$, $S_8(45)$, $S_{10}(14)$, $S_{12}(22)$
	ν_7	1060	1074	$S_5(41)$, $S_7(14)$, $S_8(42)$, $S_{11}(11)$
	ν_8	732	738	$S_6(11)$, $S_7(60)$
	ν_9	410	435	$S_5(10)$, $S_7(16)$, $S_9(52)$, $S_{10}(13)$
	ν_{10}	306	295	$S_5(21)$, $S_9(37)$, $S_{10}(29)$
	ν_{11}	125	120	$S_{10}(41)$, $S_{12}(49)$

Results

Band Assignments. The infrared spectra of (1) and (1)-d_{18} from 4000 to 400 cm^{-1} and from 400 to 100 cm^{-1} are shown respectively in Figs. 2 and 3. The Raman spectrum of (1) in the solid state is shown in Fig. 4. In normal coordinate analyses, we have approximated the methyl group as a single atom having masses of 15.035 and 18.035 for (1) and (1)-d_{18}, respectively. Thus the absorptions due to the methyl group were confirmed by comparing the spectrum of (1) with that of (1)-d_{18}. The four bands at 2970, 2935, 2892, and 2842 cm^{-1} are assigned to the C–H stretching vibrations, which disappear upon deuteration of the methyl groups. The deutero analog (1)-d_{18} shows three bands at 2370, 2235 and 2079 cm^{-1} assigned to the C–D stretching vibrations. The broad and strong absorption at 1553 cm^{-1} is mainly due to the C_3^+–N< stretching vibration and the C–C ring stretching vibration according to the potential energy distribution. However, the calculation indicates a slight shift of ν_5 upon deuteration. The observed value shows a

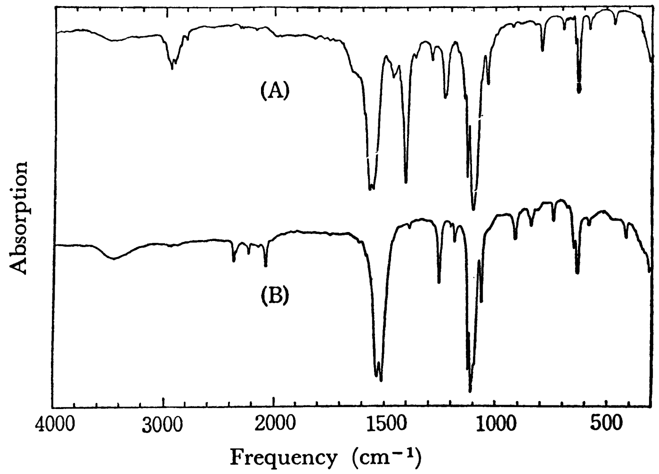


Fig. 2. Infrared spectra of trisdimethylaminocyclopropenium perchlorate (A) and its deutero analog (B).

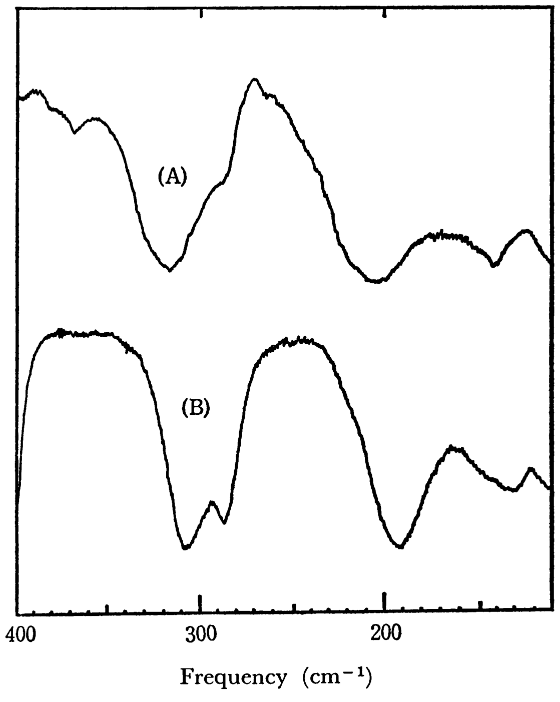


Fig. 3. Far-infrared spectrum of trisdimethylaminocyclopropenium perchlorate (A) and its deutero analog (B).

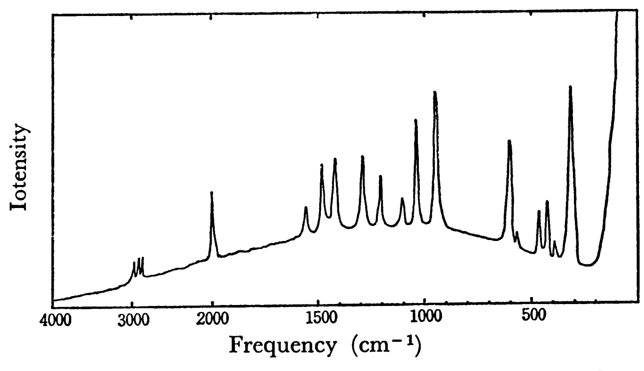


Fig. 4. Raman spectrum of trisdimethylaminocyclopropenium perchlorate.

lower frequency-shift of about 20 cm^{-1} upon deuteration. The discrepancy is attributed to the one mass approximation of the CH_3 and CD_3 groups. Breslow *et al.* reported that the degenerate ring deformation of the $C_3H_3^+$ mode appears at 1276 cm^{-1}.10) We have assigned the corresponding absorption of the $C_3(CH_3)_3^+ \cdot SbCl_6^-$ to 1490 cm^{-1} referring to the spectra of the $C_3(CD_3)_3^+ \cdot SbCl_6^-$.11)

The Raman line at 1135 cm^{-1} is assigned to the symmetric C_3^+–N⟨ stretching (ν_2) coupled with the N–CH_3 symmetric stretching (ν_3). The band at 1238 cm^{-1} is assigned to the C_3^+–N⟨ stretching vibration. The Raman line at 1985 cm^{-1} of medium intensity is assigned to the totally symmetric C–C stretching vibration S_1(C_3^+ core breathing) coupled with the C_3^+–N stretching mode (S_2). The C_3^+ core stretching (S_1) shows the largest contribution to ν_1. The calculation indicates that the coupling of the C_3^+ ring stretching vibration with the C–N⟨ stretching mode in E′ species is stronger than that in A_1' species.

The bands at 1455 and 1405 cm^{-1} of (1) are interpreted to be the CH_3 asymmetric and symmetric deformation modes. No CH_3 deformation band appears for (1)-d_{18} in this region. The two bands of (1)-d_{18} appear at 1180 and 1120 cm^{-1} as shoulder bands of the strong absorption (1100 cm^{-1}) of the ClO_4^-. A lower frequency band of the CH_3 rocking of (1) appears at 1225 cm^{-1} and 1134 cm^{-1}. The deutero compound (1)-d_{18} shows two absorptions due to the CD_3 rocking modes at 904 and 835 cm^{-1}.

The sharp band at 1060 cm^{-1} of (1)-d_{18} is explained to be the C–C stretching of the C_3^+ ring and the N–CD_3 stretching vibration. The corresponding absorption of (1) seems to shift to a slightly higher frequency region resulting in the overlapping with the strong absorption of the ClO_4^- ion. The band at 790 cm^{-1} of (1) can be assigned to the N–CH_3 stretching mode, which is confirmed by deuteration of the methyl group. The N–CD_3 stretching appears at 732 cm^{-1} in accordance with the calculation. The Raman line at 614 cm^{-1} is assigned to the symmetric N–CH_3 stretching vibration. The bands at 455, 316, and 130 cm^{-1} of (1) are assigned to the CH_3–N–CH_3 bending, the C_3^+–N–CH_3 bending and the $C_3^+N(CH_3)_2$ bending modes, respectively. The bands shift to a slightly lower frequency region upon deuteration. A weak band at 290 cm^{-1} and a band at 206 cm^{-1} are presumably due to the out-of-plane deformations of the N–$(CH_3)_2$ groups. The presence of perchlorate ion is confirmed by the bands at 1100 and 680 cm^{-1} assigned to the Cl–O stretching and bending modes of ClO_4^- ion.

Discussion

It is noted that extremely stable triaminocyclopropenium ion (1) shows the highest frequency of the totally symmetric C–C stretching vibration of the C_3^+ core among the various cyclopropenium ions reported so far (Table 5). For example, the ions $C_3(CH_3)_3^+$, $C_3(C_6H_5)_3^+$ and $C_3Cl_3^+$ exhibit the C–C stretching mode (A_1') at 1880, 1845 and 1791 cm^{-1} in their Raman spectra respectively. It is noteworthy that there is

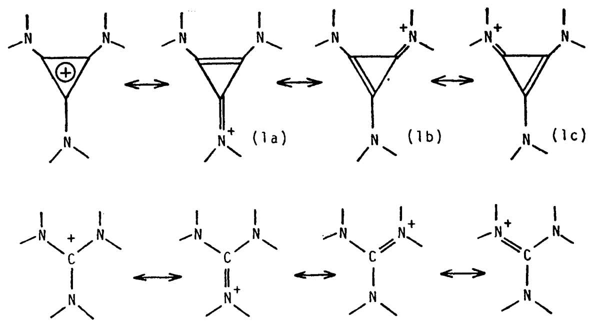
TABLE 5. FREQUENCIES OF RING DEFORMATION VIBRATION AND pK_{R^+} VALUES OF VARIOUS CYCLOPROPENIUM IONS $C_3X_3^+$

X=	H	Cl	C_6H_5	CH_3	$N(CH_3)_2$
A_1' (Raman)	—	1791[b)]	1845[c)]	1875[h)]	1985[g)]
E' (IR)	1276[a)]	1321[b)]	1411[c)]	1446[h)]	1553[g)]
pK_{R^+}	−7.4[a)]	−3[f)]	3.1[d)]	7.4[e)]	13[f)]

a) R. Breslow and J. T. Groves, *J. Amer. Chem. Soc.*, **92**, 984 (1970). b) R. West, A. Sadô and S. W. Jobey, *ibid.*, **88**, 2488 (1966). c) F. Höfler, B. Schrader, and A. Krebs, *Z. Naturforsch.*, **24a**, 1617 (1969). d) R. Breslow, J. Rockhart, and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2375 (1961). e) J. Ciabattoni and E. C. Nathan, III, *Tetrahedron Lett.*, **57**, 4997 (1969). f) Ref. 12. g) This work. h) Ref. 11.

an empirical linear relationship between the stability (pK_{R^+}) of C_3^+ core and the frequencies of the C_3^+ core vibrations (A_1' and E').[12)] The two frequencies shift towards a higher frequency region with the increase of the relative stability of the cyclopropenium ion. Although pK_{R^+} of (1) could not be determined by the usual potentiometric titration because of its alkaline hydrolysis,[5)] we could estimate this value to be 13 from the relationship between pK_{R^+} values of cyclopropenium ions and their degenerate ring deformation (Table 5). Such a remarkable stabilization of cyclopropenium ion by amino-substitution has also been observed in the case of aminodiphenylcyclopropenium ion[14)] ($pK_{R^+}=10$). The INDO calculation of triaminocyclopropenium ion suggests that its high stability is due to the large electron-donating π conjugative effect of amino group on the C_3^+ ring.[15)] Since the frequency of ring deformation vibration is sensitive to the peripheral substituent, the vibrational spectrum of highly strained cyclopropenium ion may provide an accessible and convenient method to estimate its relative stability.

Of the force constants obtained for trisdimethylaminocyclopropenium ion (Table 3), the force constant (6.62) of the C–C stretching vibration of (1) is larger than the force constants (6.22 and 6.31) of trichloro- and trimethyl-cyclopropenium ions.[11)] The values ($Cl < CH_3 < N(CH_3)_2$) seem to be strange, since electron-donating π conjugative effect of the amino group (+0.190) is larger than that of Cl- and CH_3- (+0.005) groups.[15] Since the C–C π bond order ($CH_3 > N(CH_3)_2$) of the C_3^+ ring decreases with increase in electron-donating nature of substituent, the observed increase of the ring stretching force constant ($CH_3 < N(CH_3)_2$) might be responsible for the marked increase of the C–C σ-bond order in (1). This is a peculiar property of the cyclopropenium ring. The X-ray crystallographic study[6)] of (1) indicates that the C–C bond length of (1) is about 0.01 Å shorter than that of triphenylcyclopropenium ion.[13)] The result seems to support the larger C–C stretching force constant of (1). It is possible to explain the increase in the K(C–C) on the basis of the decrease in the replusion between the carbon nuclei of the three membered ring due to the strong electron donating amino groups. It is of particular interest to compare the C–N stretching vibration of (1) with that of the guanidine hydrochloride, for which Yamaguchi[7)] assigned the infrared absorption at 1640 cm^{-1} and Raman line at 1015 cm^{-1} to the degenerate C–N stretching vibration and symmetric C–N stretching vibration, respectively. The large contribution of the $C_3^+{-}N\langle$ stretching mode to this band indicates a strong π-conjugative interaction between the amino group and the C_3^+ core. The canonical structures of (1) can be shown as above in analogy with guanidium salt. The INDO type calculation shows a considerable migration of the positive charge from the C_3^+ ring to the peripheral amino groups,[15)] suggesting a large contribution of the charge-delocalized structures (Ia, Ib, and Ic).



It is interesting to note that the C_3^+–N stretching force constant is very large and comparable to that of guanidium salt.[7)] This can be interpreted in terms of the large delocalition of the positive charge to the peripheral amino groups. The C–N bond lengths of (1) and guadinium salt obtained by X-ray analysis are 1.333 Å and 1.34 Å, respectively, which are markedly smaller than the length of the ordinary C–N single bond (*ca.* 1.47 Å). The small negative bending force constant of the C_3^+ core is derived from the transformation of the internal coordinates to the symmetry involving the redundant condition of the ring C_3^+ system.[11)]

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