

sumed value of  $\phi$  for minimum potential energy. Only a small and quite reasonable change in that parameter is required to bring the calculated value of  $V_0$  for  $S_8$  up into the range of the more directly determined values for the disulfides.

The contribution of tautomerism to the thermodynamic functions can be obtained from the partition function

$$Q = 1 + \exp[-\Delta F(D_{2d})/RT] + \exp[-\Delta F(C_1)/RT]$$

in which  $\Delta F(\text{tautomer})$  is the free-energy change for the reaction  $S_8(D_{2d}) = S_8(\text{tautomer})$ . If the energy of the  $D_{2d}$  form and of the  $C_1$  form are taken to be equal to each other and to  $V_0$ , one may write

$$Q \approx 1 + A \exp(-V_0/RT)$$

in which  $A = \exp[\Delta S(D_{2d})/R] + \exp[\Delta S(C_1)/R]$ , with  $\Delta S(\text{tautomer})$  defined as the entropy change for the reaction  $S_8(D_{2d}) = S_8(\text{tautomer})$ . If the values of  $\Delta S(\text{tautomer})$  are determined solely by differences in symmetry number and the existence of *d*- and *l*-isomers of the  $C_1$  form, then  $A = 2 + 2(8) = 18$ . Differences in moments of inertia and vibrational frequencies of the tautomers will make  $A$  differ somewhat

from 18, but that value is a good enough estimate for purposes of the present discussion.

The contributions of tautomerism to the function  $-(F^\circ - H_0^\circ)/T$ , in cal. deg.<sup>-1</sup> mole<sup>-1</sup> at 450 and 1000°K. were calculated for  $V_0$  equal to 5, 9 and 15 kcal. mole<sup>-1</sup> with the results shown below.

	$V_0 = 5$ kcal. mole <sup>-1</sup>	$V_0 = 9$ kcal. mole <sup>-1</sup>	$V_0 = 15$ kcal. mole <sup>-1</sup>
450°K.	0.14	0.002	0.000003
1000°K.	1.80	.36	.02

These values are essentially upper limits of the contributions, because  $V_0$  is the probable lower limit of the energy difference between the tautomers. It is seen that if  $V_0$  is in the expected range of 9 to 15 kcal. mole<sup>-1</sup>, the contributions of tautomerism, even at 1000°K., are of just borderline significance. Only if  $V_0$  has an improbably low value of 5 kcal. mole<sup>-1</sup> are the contributions large at temperatures near 1000°K. In either case, the contributions are small at 450°K.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

## cis- and trans-Dichloroethylenes. The Infrared Spectra from 130–400 Cm.<sup>-1</sup> and the Thermodynamic Properties<sup>1</sup>

BY KENNETH S. PITZER AND J. L. HOLLENBERG

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The infrared spectrum of *trans*-dichloroethylene shows a strong Q branch at 227 cm.<sup>-1</sup> and a shoulder of medium strength near 250 cm.<sup>-1</sup> which are interpreted as the heretofore unobserved  $A_u$  and  $B_u$  fundamentals, respectively. The spectrum of the *cis* isomer merely confirms bands known from the Raman spectrum. The force constants for out-of-plane motions are calculated. Thermodynamic functions are calculated from the completed molecular data for each isomer and are used to interpret the *cis-trans* equilibrium data. The *cis* isomer is found to be  $445 \pm 20$  cal./mole lower in energy at 0°K., and the cause of this energy difference is discussed.

In the case of the 2-butenes the *trans* isomer is known to be the one of lower energy and this is believed to be the usual case. The dichloroethylenes are an exception in that the *cis* isomer has the lower energy. Thus a careful study of *cis*- and *trans*-dichloroethylenes is of considerable interest.

The vibrational spectra of *cis*- and *trans*-dichloroethylene and the statistical thermodynamics of the equilibrium between them have been the subject of an extensive series of investigations. Recent studies of a general nature are those of Bernstein and Ramsay<sup>2</sup> and of Wood and Stevenson,<sup>3</sup> who give references to earlier work. In spite of extensive studies, the absence of infrared spectra for the *trans* isomer below about 400 cm.<sup>-1</sup> has prevented a satisfactory completion of this work. Since the *trans* molecule has a center of symmetry, the Raman spectrum does not yield the frequencies of the antisymmetric modes as fundamentals and there are two modes in the heretofore unobserved range. Attempts have been made to infer these frequencies indirectly, but we shall see that these have not yielded valid results.

**Experimental.**—The grating spectrometer employed in this investigation was described recently.<sup>4</sup>

(1) This work was assisted by the American Petroleum Institute through Research Project 50.

(2) H. J. Bernstein and D. A. Ramsay, *J. Chem. Phys.*, **17**, 556 (1949).

(3) R. E. Wood and D. P. Stevenson, *THIS JOURNAL*, **63**, 1650 (1941).

(4) C. R. Bohn, N. K. Freeman, W. D. Gwinn, J. L. Hollenberg and K. S. Pitzer, *J. Chem. Phys.*, **21**, 719 (1953).

The samples were from the Matheson Co. The sample of the *cis* isomer melted at  $-80.4^\circ$  which is within 0.1° of the accepted melting point and its infrared spectrum (3–15  $\mu$ ) showed no bands of the *trans* isomer or of other likely impurities. Consequently, this sample was used without further purification. Initially the sample of the *trans* isomer showed considerable impurity of *cis*. This was largely removed by distillation with an efficient column so that, in the sample used, the infrared spectrum showed only traces of the stronger bands of the *cis* isomer.

The spectrum of *trans*-dichloroethylene in the range 130–400 cm.<sup>-1</sup> is shown in Fig. 1. The accuracy of the percentage transmission becomes gradually poorer with decreasing frequency. While there is no doubt about the strong absorption near 230 cm.<sup>-1</sup>, the weak peak near 150 cm.<sup>-1</sup> must be regarded as doubtful at present. The corresponding spectrum was taken for the *cis* isomer, but it showed no marked features beyond the expected band at 173 cm.<sup>-1</sup> which was weak. Thus this spectrum was not investigated further.

**Spectral Interpretation.**—We accept the assignments of Bernstein and Ramsay<sup>2</sup> for *cis*-dichloroethylene and for all fundamentals except  $\mu_7(A_u)$  and  $\mu_{12}(B_u)$  of *trans*-dichloroethylene. For the latter these authors suggested 192 and 265 cm.<sup>-1</sup>, respectively, but it is apparent from Fig. 1 that these are not correct. Also we must note that the "reststrahlen" spectrometer results presented re-

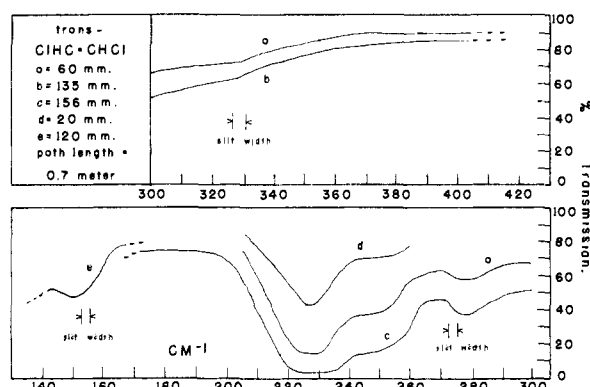


Fig. 1.—The infrared spectrum of *trans*-dichloroethylene.

cently by O'Loane<sup>5</sup> as supporting this assignment were misleading in this respect. In neither case was any error of experiment involved; rather the data allowed more than one interpretation.

From Fig. 1 it is apparent that one of the frequencies must lie at 227  $\text{cm}^{-1}$ . The relatively sharp peak suggests a strong Q branch which is characteristic of a C type vibration—in this case  $\nu_7$  of  $A_u$  symmetry.

The location of the second fundamental  $\nu_{12}$  is less obvious, but the intensity of the shoulder at about 250  $\text{cm}^{-1}$  is much greater than that of the peak at 278  $\text{cm}^{-1}$ . Also the sum of 227 + 250 = 477 is already above the range 420–450  $\text{cm}^{-1}$  regarded as most probable for the sum of  $\nu_7 + \nu_{12}$  by Wood and Stevenson<sup>3</sup> on the basis of their equilibrium data. The rather doubtful peak near 150  $\text{cm}^{-1}$  is even weaker than the others and may be definitely excluded as a fundamental. There is no explanation of bands at either 250 or 278  $\text{cm}^{-1}$  as binary combination tones, but it is possible to explain the weaker band at 278  $\text{cm}^{-1}$  as the ternary difference combination  $2\nu_{12} - \nu_7$  if  $\nu_{12}$  is taken at 250  $\text{cm}^{-1}$ .

Thus we adopt 227 and 250  $\text{cm}^{-1}$ , respectively, for  $\nu_7$  and  $\nu_{12}$ . Table I summarizes the complete assignments for both *cis* and *trans* isomers while Table II gives the full spectrum for the *trans* molecule. A comparison of our Table II with the corresponding table of Bernstein and Ramsay will show that the explanation of the weak bands as

TABLE I  
FUNDAMENTAL FREQUENCIES FOR *cis*- AND *trans*-DICHLOROETHYLENE

	<i>cis</i> , $\text{cm}^{-1}$	<i>trans</i> , $\text{cm}^{-1}$
A <sub>1</sub>	$\nu_1$ 3077	$\nu_1$ 3073
	$\nu_2$ 1587	$\nu_2$ 1578
	$\nu_3$ 1179	$\nu_3$ 1274
	$\nu_4$ 711	$\nu_4$ 846
	$\nu_5$ 173	$\nu_5$ 350
A <sub>2</sub>	$\nu_6$ 876	$\nu_6$ 895
	$\nu_7$ 406	$\nu_7$ 227
B <sub>1</sub>	$\nu_8$ 3072	B <sub>g</sub> $\nu_8$ 763
	$\nu_9$ 1294	
	$\nu_{10}$ 848	
B <sub>2</sub>	$\nu_{11}$ 571	B <sub>u</sub> $\nu_9$ 3080
	$\nu_{12}$ 697	B <sub>u</sub> $\nu_{10}$ 1200
		B <sub>u</sub> $\nu_{11}$ 817
		B <sub>u</sub> $\nu_{12}$ 250

(5) J. K. O'Loane, *J. Chem. Phys.*, **21**, 669 (1953).

overtone or combination tones is improved in almost every case where a change is made. We have substituted the Raman spectrum of Kreuzsch, Ziomek and Cleveland<sup>6</sup> for the older work used in previous assignments. Except for differences of a few  $\text{cm}^{-1}$  in some frequencies the only changes are in the polarization of the bands at 758 and 3142  $\text{cm}^{-1}$  which had been assigned in violation of older polarization data. There is complete agreement now with the recent polarization values.

TABLE II  
SPECTRA OF *trans*-DICHLOROETHYLENE

Vapor	Infrared Liquid	Raman Liquid	Assignment
227	.. (m)		$\nu_7(A_u)$
250	.. (w)		$\nu_{12}(B_u)$
278	.. (vw)		$2\nu_{12} - \nu_7 = 273(A_u)$
		350 (s) pol.	$\nu_5(A_g)$
	541 (vvw)		$\nu_8 - \nu_7 = 536(B_u)$
	614 (vvw)		$\nu_4 - \nu_7 = 619(A_u)$
		763 (m) dp.	$\nu_8(B_g)$
754 } 763 } 823 } 832 }	763 (w)		$3\nu_{12} = 750(B_u)$ , also $\nu_8$ in liq.
			$\nu_{11}(B_u)$
		846 (s) pol.	$\nu_4(A_g)$
898	895 (vs)		$\nu_8(A_u)$
	985 (w)		$\nu_8 + \nu_7 = 990(B_u)$
	1080 (w)		$\nu_4 + \nu_7 = 1073(A_u)$
	1166 (w)		$\nu_6 + \nu_{11} = 1167(B_u)$
1195 } 1205 }	1200 (s)		$\nu_{10}(B_u)$
	1276 (w)	1274 (s) pol.	$\nu_3(A_g)$
		1578 (s) pol.	$\nu_2(A_g)$
		1634 (vw) pol.	$2\nu_{11} = 1634(A_g)$
1654 } 1663 }	1658 (m)		$\nu_6 + \nu_8 = 1658(B_u)$ $\nu_4 + \nu_{11} = 1663(B_u)$
		1693 (w) pol.	$2\nu_4 = 1692(A_g)$
	1816 (w)		$\nu_2 + \nu_{12} = 1828(B_u)$
	2047 (w)		$\nu_4 + \nu_{10} = 2046(B_u)$
2092	2082 (w)		$\nu_3 + \nu_{11} = 2091(B_u)$
	2460 (w)		$\nu_8 + \nu_{10} = 2474(B_u)$ $\nu_2 + \nu_6 = 2473(A_u)$ $\nu_2 + \nu_{10} = 2778(B_u)$
	2760 (w)		
		3073 (s) pol.	$\nu_1(A_g)$
3090	3080 (s)		$\nu_9(B_u)$
		3141 (w) pol.	$2\nu_2 = 3156(A_g)$

**Bending Potential Constants.**—The potential function for out-of-plane bending motions of these molecules was considered by Freeman and one of us<sup>7</sup> and more recently by Bernstein and Ramsay.<sup>2</sup> We have revised the earlier calculations to take account of the present assignment of  $\nu_7$ . We use the "atomic weight-Ångström units" and the slightly simplified geometry used previously.<sup>7</sup> A complete harmonic potential function was assumed with  $\theta_1$  and  $\theta_2$  the wagging angles between the planes of the CHCl groups and the C-C axis and  $\theta_3$  the angle of twist of the C-C double bond.

The potential constants reduce by symmetry to four in number. The principal wagging constant,

(6) E. Kreuzsch, J. S. Ziomek and F. F. Cleveland, *Phys. Rev.*, **75**, 334 (1949). Their band at 711  $\text{cm}^{-1}$  presumably arises from an impurity of the *cis* isomer.

(7) K. S. Pitzer and N. K. Freeman, *J. Chem. Phys.*, **14**, 586 (1946).

$F_{11}$  (or  $F_{22}$ ), and the wagging interaction constant,  $F_{12}$ , are assumed to be the same for the *cis* and *trans* isomers. The principal twisting constant,  $F_{33}$ , and the twisting-wagging interaction constant,  $F_{13}$ , are evaluated for each isomer separately. The signs of the constants are as defined in an earlier paper<sup>8</sup> on the 2-butenes which also gives working equations that can readily be reduced to the case at hand. We may remark that the sign of  $F_{12}$  is such as to raise the resistance to boat-like distortions and lower it to chair-like distortions.

The resulting constants are given in Table III together with values for the 2-butenes and for ethylene. The close similarity of the constants is striking. The near equality of  $F_{33}$  for the *cis* and *trans* isomers of dichloroethylene indicates a corresponding equality of curvature at the two minima in the potential curve for torsion. The constants in Table III may be converted to the units ergs per radian<sup>2</sup> by division by  $1.698 \times 10^{11}$ .

TABLE III

BENDING POTENTIAL CONSTANTS FOR *cis*- AND *trans*-DICHLOROETHYLENE AND RELATED MOLECULES (IN ATOMIC WEIGHT-ÅNGSTRÖM UNITS)

Constant	$C_2H_2Cl_2$		$C_2H_4^a$	2-Butenes <sup>b</sup> ( <i>cis</i> and <i>trans</i> )
	<i>cis</i>	<i>trans</i>		
$F_{11}$	0.407		0.390	0.41
$F_{12}$	.048		.056	0.04
$F_{33}$	1.07	1.12	.915	1.08
$F_{13}$	-0.13	-0.14	...	-0.09

**Thermodynamic Functions.**—The functions ( $F^\circ - H^\circ_0$ )/ $T$ ,  $H^\circ - H^\circ_0$ ,  $S^\circ$  and  $C^\circ_p$  were calculated for each isomer by the usual statistical methods with the vibration frequencies of Table I. The moments of inertia were given by Bernstein and Ramsay.<sup>2</sup> Only the smallest moment of the *trans* isomer has been obtained spectroscopically, but the values from electron diffraction measurements of bond distances and angles are sufficiently accurate for our

TABLE IV

THERMODYNAMIC FUNCTIONS FOR *cis*-DICHLOROETHYLENE (UNITS, KCAL./MOLE OR CAL./DEG. MOLE)

$T$	$C^\circ_p$	$H^\circ - H^\circ_0$	$-\frac{(F^\circ - H^\circ_0)}{T}$	$S^\circ$
200	12.30	1.920	54.00	63.60
273.16	14.75	2.910	57.15	67.80
298.16	15.55	3.289	58.10	69.13
300	15.61	3.318	58.17	69.23
400	18.41	5.024	61.56	74.12
500	20.57	6.978	64.51	78.47
600	22.23	9.121	67.17	82.37
700	23.54	11.41	69.60	85.90
800	24.60	13.82	71.84	89.11
900	25.48	16.33	73.92	92.06
1000	26.23	18.91	75.87	94.79
1100	26.86	21.57	77.71	97.32
1200	27.40	24.28	79.44	99.68
1300	27.87	27.04	81.09	101.89
1400	28.27	29.85	82.65	103.97
1500	28.61	32.70	84.14	105.93

(8) J. E. Kilpatrick and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **58**, 191 (1947).

(9) R. L. Arnett and B. L. Crawford, Jr., *J. Chem. Phys.*, **18**, 118 (1950).

TABLE V

THERMODYNAMIC FUNCTIONS FOR *trans*-DICHLOROETHYLENE (UNITS, KCAL./MOLE OR CAL./DEG. MOLE)

$T$	$C^\circ_p$	$H^\circ - H^\circ_0$	$-\frac{(F^\circ - H^\circ_0)}{T}$	$S^\circ$
200	13.07	2.003	53.52	63.53
273.16	15.22	3.038	56.80	67.92
298.16	15.93	3.427	57.79	69.29
300	15.99	3.457	57.86	69.39
400	18.58	5.189	61.38	74.35
500	20.65	7.155	64.42	78.73
600	22.28	9.304	67.14	82.64
700	23.57	11.60	69.61	86.18
800	24.62	14.01	71.89	89.40
900	25.50	16.52	74.00	92.35
1000	26.24	19.11	75.97	95.08
1100	26.87	21.76	77.82	97.61
1200	27.41	24.48	79.57	99.97
1300	27.87	27.24	81.23	102.18
1400	28.27	30.05	82.80	104.26
1500	28.62	32.89	84.30	106.22

purposes. The resulting functions are given in Tables IV and V.

**Isomerization Equilibrium.**—The *cis-trans* isomerization equilibrium has been measured by several authors. Wood and Stevenson,<sup>3</sup> using iodine as a catalyst, obtained values at 30° intervals from 185° to 275°C., while Olson and Maroney<sup>10</sup> obtained values at 300 and 350°C. By using the free energy function from Tables IV and V a value of  $\Delta H^\circ_0$  for the reaction, *cis* = *trans*, can be obtained from each equilibrium measurement. These calculations are summarized in Table VI.

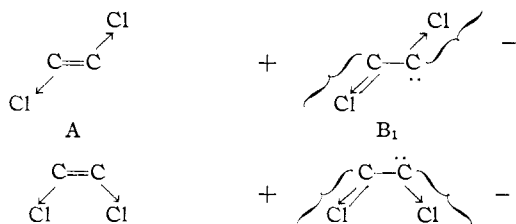
TABLE VI

$T, ^\circ K.$	ENERGY OF ISOMERIZATION $cis-C_2H_2Cl_2 = trans-C_2H_2Cl_2$			
	$K = \frac{trans}{cis}$	$\Delta F^\circ/T$	$-\Delta\left(\frac{F^\circ - H^\circ_0}{T}\right)$	$\Delta H^\circ_0$ , cal./mole
458.16	0.577	1.091	-0.126	442
488.16	.607	0.990	- .097	436
518.16	.632	.910	- .073	434
548.16	.658	.832	- .057	425
573.16	.645	.871	- .045	473
623.16	.683	.755	- .015	461
				445 ± 20

If everything is correct, the values of  $\Delta H^\circ_0$  in Table VI should be constant. Within the series of values from Wood and Stevenson there seems to be a slight trend downward with increasing temperature. The higher values of  $\Delta H^\circ_0$  from the experiments of Olson and Maroney at still higher temperatures leads us to believe this apparent trend is spurious and that these  $\Delta H^\circ_0$  values may be accepted as constant within experimental error. We select  $445 \pm 20$  cal./mole as our final value of the heat of isomerization at 0°K. The *trans* isomer has the higher energy.

**Discussion.**—While it is not practical to present any rigorous theoretical analysis of the energy of isomerization, some rough calculations seem worthwhile. The chemical bond structures which would be expected to contribute to the ground state are

(10) A. R. Olson and W. Maroney, *THIS JOURNAL*, **56**, 1320 (1934).



where there is an equivalent  $B_2$  structure in each case with the double bond to the other chlorine atom. We have used arrows to indicate the polarization of the  $\sigma$ -bonds. Since this polarization will be substantial, we have shown the formal charges shared between pairs of atoms in the B structures.

Quantitative estimates of the fraction of double bond character in mono- or dichloroethylenes have been made from the bond distance by Pauling<sup>11</sup> and from the nuclear quadrupole interactions by Goldstein and Bragg.<sup>12</sup> The respective values are 18 and 4%. This leaves a wide range of plausible values to fit another observable quantity.

In quantum mechanical calculations the energy depends on the exchange integrals as well as the coulomb integrals, but it will be a reasonable approximation to consider only the coulomb terms in discussing the *cis-trans* energy difference. The Cl-Cl distances are approximately the same in the gauche or skew form of 1,2-dichloroethane as in the *cis* form of 1,2-dichloroethylene, and similarly they are about the same in the *trans* forms of the two molecules. The values are approximately 3.25 and 4.27 Å., respectively.<sup>2,13</sup> Consequently, it seems reasonable to take the energy difference between the two forms of the ethane derivative as appropriate for the A structures. This energy difference<sup>14</sup> is about 1400 cal./mole with the *trans* form lower.

(11) L. Pauling, "The Nature of the Chemical Bond," Second edition, Cornell University Press, Ithaca, N. Y., 1945, p. 216.

(12) J. H. Goldstein and J. K. Bragg, *Phys. Rev.*, **75**, 1453 (1949); **78**, 347 (1950).

(13) O. Hassel and H. Viervoll, *Arch. Math. Naturvidenskab*, **B47**, No. 13 (1944).

(14) J. Powling and H. J. Bernstein, *THIS JOURNAL*, **73**, 1815 (1951).

We must now estimate the distribution of charge at each end of the molecule for the B structures. A reasonable but necessarily arbitrary basis is three-fourths of a unit positive charge on the doubly bonded chlorine and one-half of a negative charge on the other chlorine. We then proceed as follows

$$\psi = (1 - 2\lambda^2)^{1/2}\psi_A + \lambda(\psi_{B_1} + \psi_{B_2})$$

$$\Delta E_{c-t} = (1 - 2\lambda^2)\Delta Q^{(A)}_{c-t} + 2\lambda^2\Delta Q^{(B)}_{c-t}$$

where the delta quantities refer to *cis-trans* energy differences, the  $Q$ 's are coulomb terms, and  $\lambda^2$  is the fractional contribution of each B structure. The various crude approximations which are common in quantum mechanical valence theory have been made here.

Then we take  $\Delta Q^{(A)}_{c-t}$  to be 1400 cal./mole and

$$\Delta Q^{(B)}_{c-t} = -\frac{3}{8}e^2\left(\frac{1}{r_c} - \frac{1}{r_t}\right)$$

where  $e$  is the electronic charge and the  $r$ 's are the Cl-Cl distances in the indicated isomers.

If we take our value of -445 cal./mole for  $\Delta E_{c-t}$  we may solve these equations for  $\lambda^2$ . The result is a little less than 9% for  $\lambda^2$  which lies well within the range 4-18% indicated above. Moderate changes in the assumed charge distribution in the B structures will leave the value of  $\lambda^2$  in the range indicated.

The dipole moment of the *cis* isomer can also be discussed in a similar manner, but still further postulates must be made concerning the charge distribution in the principal structure, A. Thus we shall merely state that reasonable agreement can be obtained with parameters such as were given above.

In conclusion it seems safe to conclude that the anomalous stability of the *cis* isomer of dichloroethylene is associated with the unlike charges on the chlorine atoms in the B-type mesomeric structures.

Assistance in the calculations by Dr. James C. M. Li and Mr. Glenn Spencer is gratefully acknowledged.

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