Substituted Ethanes. IV. The Rotational Isomers of 1,1,2,2Tetrachloroethane: Assignments to the Normal Vibrations

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TABLE VI. Vibrational frequencies of ozone and isotopic ozone.

	O_3^{16} Observed frequency[a] (cm^{-1})	$O^{16}O^{18}O^{16}$ Calculated frequency[b] (cm^{-1})	$O^{16}O^{16}O^{18}$ Calculated frequency[b] (cm^{-1})
ν_1	1110	1080	1095
ν_2	705	697	688
ν_3	1043	1008	1029

[a] Measured by Badger and Wilson.
[b] Calculated using force constants in last column of Table II.

possible unambiguous assignment of rotational transitions of other isotopic ozone molecules.

Infrared data on isotopic ozone can also be used to check the calculated force constants. Unfortunately, no such data have been reported to date. Nevertheless, the vibration frequencies of $O^{16}O^{16}O^{18}$ and $O^{16}O^{18}O^{16}$ have been calculated and are listed in Table VI.

It must be emphasized that the ultimate accuracy of the potential function is limited by a number of factors. These include neglect of anharmonicity, use of "effective" instead of equilibrium moments of inertia, the accuracy of infrared measurements which are used to obtain interrelations among the force constants, and neglect of the inertia defect in obtaining relations among the seven nonvanishing τ's.

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Substituted Ethanes. IV. The Rotational Isomers of 1,1,2,2-Tetrachloroethane: Assignments to the Normal Vibrations

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The wave numbers of the normal vibrations of *trans* 1,1,2,2-tetrachloroethane and some of the fundamentals of the deuterated molecule were calculated by the Wilson *FG* matrix method. The infrared spectrum of 1,1,2,2-tetrachloroethane has been obtained from 530 to 4000 K (K=kayser=cm^{-1}). Complete assignments of all the observed Raman and infrared bands have been made and some unobserved fundamentals have been computed.

INTRODUCTION

KAGARISE and Rank[1] (KR) determined the rotational isomers of 1,1,2,2-tetrachloroethane to be *trans* (C_{2h}) and *gauche* (C_2). Complete assignment of the observed Raman and infrared wave numbers to the various symmetry types could not be made by KR because of the incompleteness of their infrared spectrum in the KBr region, the lack of data showing the temperature dependence of the intensities of the infrared bands, and their observance of a smaller number of Raman lines than are allowed by the selection rules.

The difficulties encountered in attempts[1,2] to obtain satisfactory infrared intensity-temperature measurements for 1,1,2,2-tetrachloroethane make it unlikely that this information will be available soon. In this work the wave numbers of the normal vibrations of the *trans*-isomer were computed in an effort to complete the assignment of the observed Raman displacements and infrared bands.

EXPERIMENTAL DATA

With the exception of the Raman displacements in brackets or parentheses, all the Raman data in Table I[3] for 1,1,2,2-tetrachloroethane was obtained by KR.[1] The 4 values in brackets were reported by Langseth and Bernstein[4] (LB) who also published the Raman data for the deuterated molecules. These bracketed Raman displacements were not verified in any of 9 other investigations,[1,5–11] including the present one. The 2 Raman displacements in parentheses were reported in 3 separate investigations.[8,10,11] In the first column, + means that the Raman line intensity increases with a decrease in temperature and hence belongs to the more stable

[1] R. E. Kagarise and D. H. Rank, Trans. Faraday Soc. 48, 394 (1952).
[2] F. E. Malherbe and H. J. Bernstein, J. Am. Chem. Soc. 74, 1859 (1952).
[3] In accord with the recommendation of the Joint Commission for Spectroscopy, σ is used as the symbol for wave number and K (kayser) is used for the wave number unit. See J. Opt. Soc. Am. 43, 410 (1953); Spec. Mol. 3, 67 (1954).
[4] A. Langseth and H. J. Bernstein, J. Chem. Phys. 8, 410 (1940).
[5] P. Pringsheim and B. Rosen, Z. Physik 50, 741 (1928).
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[7] W. Hanle, Ann. Physik 15, 345 (1932).
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[9] B. Trumpy, Z. Physik 93, 624 (1935).
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[11] R. Ananthakrishnan, Proc. Indian Acad. Sci. 5A, 285 (1937).

TABLE I. Raman and infrared spectral data and assignments for liquid 1,1,2,2-tetrachloroethane.[a]

Temp. depend.	$Cl_2HC–CHCl_2$ Raman			Infrared		$Cl_2DC–CDCl_2$ Raman			Assignment		Isomer
	$\Delta\sigma$	ρ	I	σ	σ_c	$\Delta\sigma$	I	σ_c	σ	type	
$\pm$	91	D	5			88.2	6		σ_{10}	a	gauche
					116				σ_9	a_u	trans
+	175	0.73	2.5			172.6	3		σ_9	a	gauche
	[183.6]					180.4	1		$\{2\sigma_{10}$	A_g	trans
									$2\sigma_{10}$	A	gauche
−	224	0.52	1.2		186	226.2	2	186	σ_6	a_g	trans
+	240	0.78	3			239.8	5		σ_8	a	gauche
					281				σ_{18}	b_u	trans
+	287	0.86	4	290		287.1	5		σ_{18}	b	gauche
−	298	$P?$	0.8		286	295.1	2	284	σ_{13}	b_g	trans
	(325)			326					σ_{17}	b	gauche
+	353	0.22	10	352		350.2	7		σ_7	a	gauche
				359					σ_{17}	b_u	trans
−	366	0.13	4.5	368		362.1	3	367	σ_5	a_g	trans
	(399)								σ_{16}	b	gauche
+	546	0.86	2	545		531.2	2		σ_{15}	b	gauche
				580					$\{\sigma_7+\sigma_8$	A	gauche
									$2\sigma_{18}$	A	gauche
+	648	0.03	6	651		628.0	7		σ_6	a	gauche
				714					$\sigma_9+\sigma_{15}$	B	gauche
				738	720				σ_{16}	b_u	trans
				754					$\sigma_8+\sigma_{15}$	B	gauche
−	765	0.17	2.5	792		703.1	2	698	σ_4	a_g	trans
+	801	0.58	6.5	795		741.0	8		σ_5	a	gauche
				803					σ_8	a_u	trans
−	811	0.58	2	822		758.1	2	763	σ_{12}	b_g	trans
				873					$\{\sigma_4+\sigma_9$	A_u	trans
									$\sigma_6+\sigma_8$	A	gauche
									$\sigma_5+\sigma_{10}$	A	gauche
									$\sigma_{15}+\sigma_{17}$	A	gauche
				906					$\{\sigma_9+\sigma_{12}$	B_u	trans
									$\sigma_{10}+\sigma_{12}$	B_u	trans
									Impurity?		
				929					$\{\sigma_{15}+\sigma_{16}$	A	gauche
									$\sigma_6+\sigma_{18}$	B	gauche
					961	772.1	1	794	σ_3	a_g	trans
				973					$\{\sigma_{14}$	b	gauche
									$\sigma_5+\sigma_9$	A	gauche
									$\sigma_6+\sigma_{17}$	B	gauche
+	1018	0.28	0.4	1017		829.8	2		σ_4	a	gauche
	[1028.1]								$\sigma_6+\sigma_{12}$	B_g	trans
				1087					$2\sigma_{15}$	A	gauche
	[1118]			1109		886.3	1		σ_{13}	b	gauche
	[1171]			1188	1194				σ_{15}	b_u	trans
				1201	1207				σ_7	a_u	trans
				1211		938.0	1	936	σ_{11}	b_g	trans
−	1204	0.86	0.4			950.6	2		σ_{12}	b	gauche
+	1216	0.86	1.2	1215		1006.6	1		σ_3	a	gauche
+	1242	0.56	0.4	1242		1100.0	1		σ_2	a	gauche
+	1279	0.86?	0.2	1278					σ_2	a_g	trans
−	1306	0.28	0.4		1364			1265			
				1306					$\{\sigma_4+\sigma_{18}$	B	gauche
									$\sigma_9+\sigma_{11}$	B_u	trans
				1336					$\sigma_5+\sigma_{15}$	B	gauche
				1447					$\sigma_2+\sigma_9$	A	gauche
				1598					$\{2\sigma_6$	A	gauche
									$\sigma_8+\sigma_{12}$	B_u	trans
				2031					$\{2\sigma_4$	A	gauche
									$\sigma_3+\sigma_5$	A	gauche
									$\sigma_2+\sigma_{16}$	B_u	trans
				2071					$\{\sigma_2+\sigma_5$	A	gauche
									$\sigma_{13}+\sigma_{14}$	A	gauche
				2387					$\{\sigma_2+\sigma_{13}$	B	gauche
									$\sigma_7+\sigma_{11}$	B_u	trans
				2423					$\{2\sigma_{12}$	A	gauche
									$\sigma_3+\sigma_{12}$	B	gauche
				2473					$\{2\sigma_3$	A	gauche
									$\sigma_2+\sigma_{12}$	B	gauche
									$\sigma_2+\sigma_{15}$	B_u	trans
				2511					$\sigma_2+\sigma_7$	A_u	trans
				2551					$2\sigma_2$	A	gauche

[a] $\Delta\sigma$ = Raman displacement in K (kaysers, cm⁻¹); I = relative intensity; ρ = depolarization factor (P = polarized, D = depolarized); σ = infrared wave number at point of maximum absorption; σ_c = calculated wave number; and temp. depend. = temperature dependence (see text).

TABLE I.—*Continued.*

Temp. depend.	Cl$_2$HC−CHCl$_2$ Raman			Infrared		Cl$_2$DC−CDCl$_2$ Raman			σ	Assignment type	Isomer
	Δσ	ρ	I	σ	σc	Δσ	I	σc			
±	2986	0.20	4	2980	⎰3003 ⎱3002	2233.1	2	2244	σ$_1$	a_g	*trans*
									σ$_{14}$	b_u	*trans*
						2240.9	6		⎰σ$_1$	a	*gauche*
									⎱σ$_{11}$	b	*gauche*
				3513					⎰σ$_{11}$+σ$_{15}$	A	*gauche*
									⎱σ$_1$+σ$_{15}$	B	*gauche*
				3609					⎰σ$_1$+σ$_6$	A	*gauche*
									⎱σ$_6$+σ$_{11}$	B	*gauche*
				3659					σ$_1$+σ$_{16}$	B_u	*trans*
				3747					⎰σ$_1$+σ$_5$	A	*gauche*
									⎱σ$_5$+σ$_{11}$	B	*gauche*

isomer (*gauche*), while − indicates a line of the *trans*-isomer, i.e., the Raman line decreases in intensity as the temperature is lowered. This intensity-temperature dependence given by KR[1] is confirmed in general by the Raman spectrum of the solid reported by Mizushima *et al.*,[10] as well as by the measurements of LB[4] on the liquid.

The infrared spectral data given in Table I was obtained in the present study, except for 290, 326, and 352 K which are from Plyler.[12] Figures 1 and 2 show the infrared spectrum as obtained with Beckman IR-2 (KBr) and Perkin-Elmer Model 21 (NaCl) spectrophotometers, respectively. This spectrum differs somewhat from that reported by the University of California group.[13]

CALCULATION OF FUNDAMENTALS

Potential energy constants from earlier work on methyl chloroform[14] (H$_3$C−CCl$_3$) and trichloromethanes[15] were used in a general quadratic potential function to compute (Wilson *FG* matrix method) the 6 a_g, 5 b_u, 3 b_g, and 3 of the 4 a_u fundamentals of the *trans*-isomer. The a_u torsional fundamental was not computed. The a_g and b_g fundamentals for the deuterated molecule also were computed. Except for f_{mh} all the constants
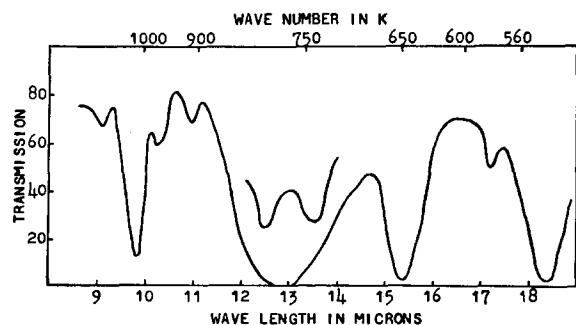

FIG. 1. Infrared spectrum of 1,1,2,2-tetrachloroethane, Beckman IR-2 (KBr), cell length *ca* 0.15 mm.

[12] E. K. Plyler, J. Chem. Phys. **17**, 218 (1949).
[13] American Petroleum Institute Infrared Spectrogram No. 1171–1172, University of California.
[14] El-Sabban, Meister, and Cleveland, J. Chem. Phys. **19**, 855 (1951).
[15] Zietlow, Cleveland, and Meister, J. Chem. Phys. **18**, 1076 (1950).

given in Table II were transferred unchanged. In the present listing the bond length multipliers of the angle constants are not carried as separate factors. The potential constants are expressed in the descriptive notation introduced by Davis *et al.*[16] The atomic masses and bond lengths are those given earlier,[15] plus C−C = 1.54 A. Decius' Tables[17] were used to compute the inverse kinetic energy matrix elements, and all angles were assumed to be tetrahedral. The symmetry coordinates are:

a_g: $R_1 = \Delta m$,

$R_2 = (1/2)(\Delta c_1 + \Delta c_2 + \Delta c_3 + \Delta c_4)$,

$R_3 = (\sqrt{2}/2)(\Delta h_1 + \Delta h_2)$,

$R_4 = (\sqrt{3}/6)(2\Delta c_1 c_2 + 2\Delta c_3 c_4$
$\quad - \Delta c_3 h_2 - \Delta c_1 h_1 - \Delta c_4 h_2 - \Delta c_2 h_1)$,

$R_5 = (\sqrt{3}/6)(2\Delta m h_1 + 2\Delta m h_2$
$\quad - \Delta m c_1 - \Delta m c_2 - \Delta m c_3 - \Delta m c_4)$,

$R_6 = (\sqrt{3}/6)(\Delta m h_1 + \Delta m h_2 + \Delta m c_1 + \Delta m c_2$
$\quad + \Delta m c_3 + \Delta m c_4 - \Delta c_1 c_2 - \Delta c_3 c_4$
$\quad - \Delta c_3 h_2 - \Delta c_1 h_1 - \Delta c_4 h_2 - \Delta c_2 h_1)$,

$R_7 = (\sqrt{3}/6)(\Delta m h_1 + \Delta m h_2 + \Delta m c_1 + \Delta m c_2$
$\quad + \Delta m c_3 + \Delta m c_4 + \Delta c_1 c_2 + \Delta c_3 c_4$
$\quad + \Delta c_3 h_2 + \Delta c_1 h_1 + \Delta c_4 h_2 + \Delta c_2 h_1) \equiv 0$.

b_g: $R_1 = (1/2)(\Delta c_1 + \Delta c_4 - \Delta c_2 - \Delta c_3)$,

$R_2 = (1/2)(\Delta m c_1 - \Delta m c_2 - \Delta m c_3 + \Delta m c_4)$,

$R_3 = (1/2)(\Delta c_3 h_2 + \Delta c_2 h_1 - \Delta c_1 h_1 - \Delta c_4 h_2)$.

a_u: $R_1 = (1/2)(\Delta c_1 - \Delta c_2 + \Delta c_3 - \Delta c_4)$,

$R_2 = (1/2)(\Delta m c_1 - \Delta m c_2 + \Delta m c_3 - \Delta m c_4)$,

$R_3 = (1/2)(\Delta c_3 h_2 + \Delta c_1 h_1 - \Delta c_4 h_2 - \Delta c_2 h_1)$,

$R_4 = \Delta \tau$.

b_u: $R_1 = (1/2)(\Delta c_1 + \Delta c_2 - \Delta c_3 - \Delta c_4)$,

$R_2 = (\sqrt{2}/2)(\Delta h_1 - \Delta h_2)$,

$R_3 = (\sqrt{3}/6)(2\Delta c_1 c_2 - 2\Delta c_3 c_4$
$\quad - \Delta m c_1 - \Delta m c_2 + \Delta m c_3 + \Delta m c_4)$,

$R_4 = (\sqrt{3}/6)(2\Delta m h_1 - 2\Delta m h_2$
$\quad + \Delta c_3 h_2 - \Delta c_1 h_1 + \Delta c_4 h_2 - \Delta c_2 h_1)$,

[16] Davis, Cleveland, and Meister, J. Chem. Phys. **20**, 454 (1952).
[17] J. C. Decius, J. Chem. Phys. **16**, 1025 (1948).
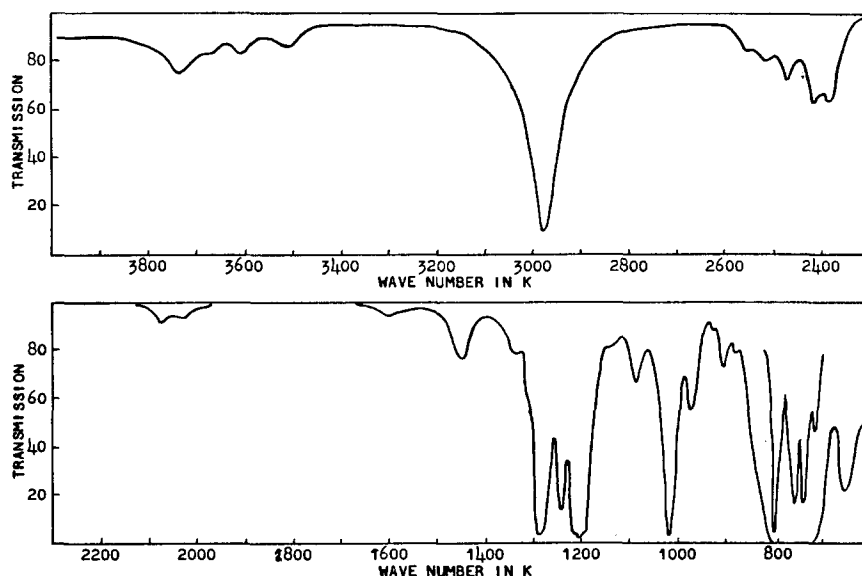
FIG. 2. Infrared spectrum of 1,1,2,2-tetrachloroethane, Perkin-Elmer 21 (NaCl), cell length 0.11 mm.

$$R_5 = (\sqrt{3}/6)(\Delta c_3 h_2 - \Delta c_1 h_1 + \Delta c_4 h_2 - \Delta c_2 h_1$$
$$+ \Delta c_1 c_2 - \Delta c_3 c_4 + \Delta m c_1 + \Delta m c_2$$
$$- \Delta m c_3 - \Delta m c_4 - \Delta m h_1 + \Delta m h_2),$$
$$R_6 = (\sqrt{3}/6)(\Delta c_3 h_2 - \Delta c_1 h_1 + \Delta c_4 h_2 - \Delta c_2 h_1$$
$$- \Delta c_1 c_2 + \Delta c_3 c_4 - \Delta m c_1 - \Delta m c_2$$
$$+ \Delta m c_3 + \Delta m c_4 - \Delta m h_1 + \Delta m h_2) \equiv 0.$$

DISCUSSION

The calculation indicates that the 811 K Raman line is b_g. The observed depolarization factor (0.58) may be in error because of the close proximity of the strong 801 K Raman line. The most serious disagreement between calculated and observed values is for 224 K (a_g). By varying potential constants, one can obtain closer agreement between this observed value (224 K) and the computed value (186 K), but only at the expense of the agreement between the observed and calculated values of the 366 and 765 fundamentals. The calculated value of 186 K is close to the 183.6 line, found only by LB,[4] whose intensity-temperature measurements place it among the lines of the less stable isomer. However, alternative explanations for the appearance of the 224 K

line are not convincing. There is no evidence to indicate that it is due to an impurity and the possibility that it is $2\sigma_9$ (*trans*) is unlikely since its relative intensity is higher than is usually the case for an overtone in the Raman spectrum.

The infrared band at 973 K is assigned as a fundamental of the *gauche*-molecule. This band was selected rather than the 873 or 929 K bands because the latter are relatively very weak. All or part of the absorption at 906 K may be due to an impurity (decomposition product ?) since there were significant relative intensity differences between two "purified" samples. However, the 906 band is numerically a more attractive choice for a C−Cl stretching vibration than is 973 K, and hence cannot be conclusively excluded as a fundamental.

TABLE II. Potential constants used in the computation of the fundamentals of the *trans*-isomers.[a]

	md/A		md/rad		md A/rad²
f_c	3.4580[b]	$f_c{}^{cc}$	0.36434	f_{cc}	1.1621
$f_c{}^c$	0.30760	$f_h{}^{cc}$	0.31922	$f_{cc}{}^{ch}$	0.028235
f_m	4.5000	$f_h{}^{ch}$	−0.31922	f_{mh}	0.30785
f_h	4.8002	$f_h{}^{mh}$	0.13180	f_{mc}	1.1998
$f_m{}^c$	0.37576	$f_c{}^{mc}$	0.37059	$f_{mc}{}^{mc}$	0.34002
$f_c{}^h$	0.08800	$f_c{}^{mc}$	−0.18529	$f_{mc}{}^{cc}$	0.12785
		$f_c{}^{ch}$	−0.16400	f_{ch}	0.92126
		$f_c{}^{ch}$	0.18601	$f_{ch}{}^{ch}$	0.27305

[a] md/A = millidyne/angstrom; rad = radian.
[b] This number of significant figures was required in earlier work (reference 15) to secure the best fit of calculated wave numbers.

TABLE III. The wave numbers of the fundamental vibrations of *trans* and *gauche*, deuterated and nondeuterated, 1,1,2,2-tetrachloroethane.[a]

Type	Trans (CHCl₂)₂ Obs	Calc	(CDCl₂)₂ Obs	Calc	Type	Gauche (CHCl₂)₂ Obs	(CDCl₂)₂ Obs
a_g: σ_1	2986	3003	2233.1	2244	a: σ_1	2983	2240.9
σ_2	1306	1364		1265	σ_2	1279	1100.0
σ_3		961	772.1	794	σ_4	1018	829.8
σ_4	765	792	703.1	698	σ_5	650	628.0
σ_5	366	368	362.1	367	σ_7	353	350.2
σ_6	224	186	226.2	186	σ_8	240	239.8
a_u: σ_7	1201	1207			σ_3	1242	1006.6
σ_8	795	803			σ_6	798	741.0
σ_9		116			σ_9	175	172.6
σ_{10}					σ_{10}	91	88.2
b_g: σ_{11}	1204	1211	938.0	936	b: σ_{12}	1216	950.6
σ_{12}	811	822	758.1	763	σ_{14}	973	
σ_{13}	298	286	295.1	284	σ_{17}	326	
b_u: σ_{14}	2980	3002			σ_{11}	2983	2240.9
σ_{15}	1188	1194			σ_{13}	1109	886.3
σ_{16}	738	720			σ_{15}	546	531.2
σ_{17}	352	359			σ_{16}	399	
σ_{18}	290	281			σ_{18}	289	287.1

[a] Refer to Table I for sources of observed data. Wave numbers are in kaysers. Obs = observed, Calc = calculated.

Teller-Redlich product rule tests of the a and b_g assignments given in Table III are satisfactory, since these ratios are less than the theoretical values by only *ca* 1.5%. For the a_g deuterated and nondeuterated wave numbers this low 1.5% discrepancy is obtained if the 1265 calculated value (C—C—D bending) is reduced to 1205 K. That this calculated value is too high is not unexpected when one considers the calculated (1364 K) and observed (1306 K) wave numbers for the C—C—H bending vibration.

For the nondeuterated molecules, the sum rule for rotational isomers[18] gives

$$\sum \sigma_i{}^2(gauche) = 2.759 \cdot 10^7$$

and

$$\sum \sigma_i{}^2(trans) = 2.765 \cdot 10^7,$$

so that the assignments are not inconsistent with this check. The wave numbers used to obtain the above sums are: *gauche*, a (91, 175, 240, 353, 650, 798, 1018, 1242, 1279, 2983), b (289, 326, 399, 546, 973, 1109, 1216, 2983); *trans*, a_g (224, 366, 765, 961, 1306, 2986), a_u (91, 116, 795, 1201), b_g (298, 811, 1204), b_u (290, 352, 738, 1188, 2980). When 906 is used instead of 973 as a b fundamental, the sum of the squared wave numbers is $2.747 \cdot 10^7$.

The sum rule of Bernstein and Pullin,[19] which appears to have some empirical validity, yields

$$\sum \sigma_i(gauche) = 16\ 670$$

and

$$\sum \sigma_i(trans) = 16\ 672.$$

ACKNOWLEDGMENTS

[18] Mizushima, Shimanouchi, Nakagawa, and Miyake, J. Chem. Phys. **21**, 215 (1953).

[19] H. J. Bernstein and A. D. E. Pullin, J. Chem. Phys. **21**, 2188 (1953).