

Substituted Propanes

Part X. 2,2-Dicyano-, 2,2-Difluoro-, and 2,2-Diiodopropane

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Harmonic force fields are given for 2,2-dicyanopropane and 2,2-difluoropropane. They are presented as F matrices in terms of thoroughly specified symmetry coordinates. For the cyano compound the analysis was based on experimental data not published previously. The similar analysis was performed tentatively for 2,2-diiodopropane, for which the available spectral data are incomplete. A set of predicted vibrational frequencies is proposed. The developed force fields were used to calculate mean amplitudes of vibration and perpendicular amplitude correction coefficients.

This work is a continuation of the systematic studies of spectra and structures of substituted propanes. It deals with 2,2-dicyano-, 2,2-difluoro-, and 2,2-diiodopropane. The related molecules 2,2-dichloro- and 2,2-dibromopropane were studied extensively before.^{1,2} Also the monosubstituted molecules 2-chloro-, 2-bromo-, 2-iodo-, and 2-cyanopropane^{3,4} are of relevance to the present work.

A normal coordinate analysis was performed for 2,2-dicyanopropane using recent spectral data not published previously. The developed harmonic force field was used to calculate the mean amplitudes of vibration⁵ and perpendicular amplitude correction coefficients.⁵ These quantities are of great interest in modern gas electron diffraction investigations (see, *e.g.*, Ref. 6). The corresponding analysis was also performed for 2,2-difluoropropane using spectral data from recent literature.^{7,8} For 2,2-diiodopropane the available spectral data are very incomplete. From the present analysis we have tentatively produced a set of predicted vibrational frequencies for this molecule.

A precise definition of the applied symmetry coordinates is given. This seems to be well justified because a set of independent internal coordinates for the molecular vibrations is very important as the basis of the force field documentations.

MOLECULAR MODELS

The molecular symmetry of propane (C_{2v}) is maintained under the 2,2-disubstitutions. Fig. 1 shows the 2,2-dicyanopropane model. The same model is applicable to propane type molecules on neglecting the atoms number 12 and 13.

VALENCE COORDINATES

The notation for valence coordinates was adopted from the analysis of the propane molecular model by Vizi and Cyvin⁹ and supplemented with the new coordinate types pertaining to the cyano groups. The former set is briefly summarized below.

(i) Two CX stretchings d . (ii) Two CC stretchings r . (iii) Two CH stretchings s in the skeleton plane. (iv) Four CH stretchings t involving H atoms outside the skeleton plane. (v) The CCC bending α . (vi) Four CCX bendings β . (vii) Four HCH bendings γ , where one of the H atoms lies in the skeleton plane and the other is outside. (viii) Four CCH bendings δ , where the H atom is outside the skeleton plane. (ix) Two CCH bendings ε , where H lies in the skeleton plane. (x) Two CCCH torsions, τ , where H lies in the skeleton plane.

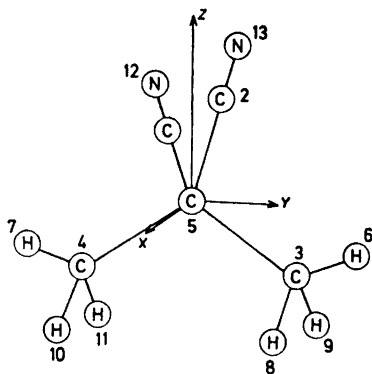


Fig. 1. The 2,2-dicyanopropane molecule model.

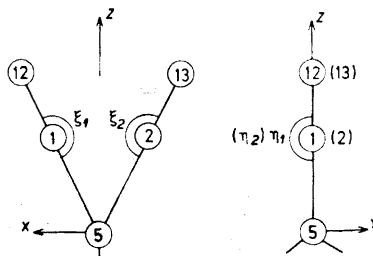


Fig. 2. Definition of the linear bending coordinates in the 2,2-dicyanopropane molecule model.

When dealing with the 2,2-dicyanopropane model the X atoms become carbon atoms of the cyano groups. The following valence coordinates are defined in addition to those summarized above.

- (xi) Two CN stretchings: p_1, p_2 for the atoms 1–12 and 1–13, respectively.
 (xii) Two linear bendings CCN in the XCX plane: ξ_1, ξ_2 for the atoms 5–1–12 and 5–2–13, respectively (see Fig. 2).
 (xiii) Two linear bendings CCN perpendicular to the XCX plane: η_1 (5–1–12) and η_2 (5–2–13) (see Fig. 2).

SYMMETRY COORDINATES

The valence coordinates were used to construct a complete set of independent symmetry coordinates. For the 2,2-dicyanopropane type molecules, the normal modes are distributed according to

$$\Gamma_{\text{vib}}(2,2\text{-dicyanopropane}) = 11A_1 + 6A_2 + 8B_1 + 8B_2$$

The present scheme of symmetry coordinates (see below) is also applicable to propane type molecules. We have namely chosen the sequence of symmetry coordinates in such a way that the particular ones pertaining to the 2,2-dicyanopropane model within each species are added at the end. For propane type molecules, one only has to apply the appropriate number of symmetry coordinates belonging to the different species in accord with the symmetric structure:

$$\Gamma_{\text{vib}}(\text{propane}) = 9A_1 + 5A_2 + 6B_1 + 7B_2$$

Species A₁:

$$\begin{aligned} S_1(A_1) &= 2^{-1/2}(d_1 + d_2) \\ S_2(A_1) &= 2^{-1/2}(r_1 + r_2) \\ S_3(A_1) &= 2^{-1/2}(s_1 + s_2) \\ S_4(A_1) &= \frac{1}{2}(t_1 + t_2 + t_3 + t_4) \\ S_5(A_1) &= R\alpha \\ S_6(A_1) &= \frac{1}{2}(RD)^{1/2}(\beta_1 + \beta_2 + \beta_3 + \beta_4) \\ S_7(A_1) &= \frac{1}{2}(ST)^{1/2}(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4) \\ S_8(A_1) &= \frac{1}{2}(RT)^{1/2}(\delta_1 + \delta_2 + \delta_3 + \delta_4) \\ S_9(A_1) &= (RS/2)^{1/2}(\varepsilon_1 + \varepsilon_2) \\ S_{10}(A_1) &= 2^{-1/2}(p_1 + p_2) \\ S_{11}(A_1) &= (DP/2)^{1/2}(\xi_1 + \xi_2) \end{aligned}$$

Species A₂:

$$\begin{aligned} S_1(A_2) &= \frac{1}{2}(t_1 - t_2 - t_3 + t_4) \\ S_2(A_2) &= \frac{1}{2}(RD)^{1/2}(\beta_1 - \beta_2 - \beta_3 + \beta_4) \\ S_3(A_2) &= \frac{1}{2}(ST)^{1/2}(\gamma_1 - \gamma_2 - \gamma_3 + \gamma_4) \\ S_4(A_2) &= \frac{1}{2}(RT)^{1/2}(\delta_1 - \delta_2 - \delta_3 + \delta_4) \\ S_5(A_2) &= (RS/2)^{1/2}(\tau_1 + \tau_2) \\ S_6(A_2) &= (DP/2)^{1/2}(\eta_1 - \eta_2) \end{aligned}$$

Species B₁:

$$\begin{aligned} S_1(B_1) &= 2^{-1/2}(d_1 - d_2) \\ S_2(B_1) &= \frac{1}{2}(t_1 - t_2 + t_3 - t_4) \\ S_3(B_1) &= \frac{1}{2}(RD)^{1/2}(\beta_1 - \beta_2 + \beta_3 - \beta_4) \\ S_4(B_1) &= \frac{1}{2}(ST)^{1/2}(\gamma_1 - \gamma_2 + \gamma_3 - \gamma_4) \\ S_5(B_1) &= \frac{1}{2}(RT)^{1/2}(\delta_1 - \delta_2 + \delta_3 - \delta_4) \\ S_6(B_1) &= (RS/2)^{1/2}(\tau_1 - \tau_2) \\ S_7(B_1) &= 2^{-1/2}(p_1 - p_2) \\ S_8(B_1) &= (DP/2)^{1/2}(\xi_1 - \xi_2) \end{aligned}$$

Species B_2 :

$$\begin{aligned} S_1(B_2) &= 2^{-1/2}(r_1 - r_2) \\ S_2(B_2) &= 2^{-1/2}(s_1 - s_2) \\ S_3(B_2) &= \frac{1}{2}(t_1 + t_2 - t_3 - t_4) \\ S_4(B_2) &= \frac{1}{2}(RD)^{1/2}(\beta_1 + \beta_2 - \beta_3 - \beta_4) \\ S_5(B_2) &= \frac{1}{2}(ST)^{1/2}(\gamma_1 + \gamma_2 - \gamma_3 - \gamma_4) \\ S_6(B_2) &= \frac{1}{2}(RT)^{1/2}(\delta_1 + \delta_2 - \delta_3 - \delta_4) \\ S_7(B_2) &= (RS/2)^{1/2}(\varepsilon_1 - \varepsilon_2) \\ S_8(B_2) &= (DP/2)^{1/2}(\eta_1 + \eta_2) \end{aligned}$$

Here the capital letters R , D , S , T , and P are used in scaling factors and designate the equilibrium distances of C-C(methyl), C-C(cyano), C-H (in skeleton plane), C-H (out of skeleton plane) and C \equiv N, respectively.

The symmetry coordinate set for the propane model, which is a part of the above set, is identical to the symmetry coordinate set given elsewhere.⁹ It was used previously as the basis of symmetry force constants for propane,^{2,10} 2,2-dichloropropane,² and 2,2-dibromopropane.²

2,2-DICYANOPROPANE (DIMETHYLMALONITRILE)

The $(\text{CH}_3)_2\text{C}(\text{CN})_2$ and $(\text{CD}_3)_2\text{C}(\text{CN})_2$ molecules were investigated by infrared and Raman spectroscopy¹¹ as a part of systematic studies of substituted malonitriles. A report of the experimental part is to be published elsewhere. That work was performed parallel with the present analysis, and initial force constant calculations were used as an aid in the assignment of the experimental frequencies.

An initial force field was constructed by transferring the force constants from related molecules.^{2,4} It seems not to be of interest to report any details of the different steps of iteration in the refinements of the force field. The final force constants (see Table 1) were adjusted so as to fit accurately the experimental frequencies for $(\text{CH}_3)_2\text{C}(\text{CN})_2$. They are (in cm^{-1}): (A_1) 3004, 2951, 2252, 1443, 1397, 1197, 951, 665, 580, 510, and 150; (A_2) 3004, 1459, 1020, 351, 236 and 204; (B_1) 3004, 2252, 1472, 1224, 1128, 468, 320, and 282; (B_2) 3004, 2951, 1459, 1376, 1224, 951, 390, and 195. The calculated frequencies for $(\text{CD}_3)_2\text{C}(\text{CN})_2$ from the final force field are: (A_1) 2270, 2242, 2128, 1136, 1078, 1030, 785, 622, 508, 490, and 149; (A_2) 2247, 1042, 798, 339, 187, and 167; (B_1) 2277, 2230, 1356, 931, 876, 444, 281, and 221; (B_2) 2245, 2128, 1229, 1066, 984, 743, 372, and 185. The frequencies for the deuterated compound were found to be generally in satisfactory agreement with the observed values.¹¹ A detailed discussion of the assignment of the experimental frequencies is postponed to the coming publication.

The final force field is given in Table 1 in terms of the symmetry F matrix blocks. It was used to calculate the mean amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K).^{5,6,12} The results for all the twenty-eight interatomic distance types in $(\text{CH}_3)_2\text{C}(\text{CN})_2$ at the temper-

Table 1. Symmetry force constants (mdyn/Å) for 2,2-dicyanopropane.

Species A_1									
1	6.24								
2	0.48	3.83							
3	-0.03	-0.03	4.82						
4	0.04	-0.03	0.12	4.91					
5	-0.41	0.29	-0.05	0.03	1.19				
6	-0.11	0.05	-0.01	0.01	0.18	1.80			
7	0.07	0.01	-0.04	0.03	-0.04	0.03	1.27		
8	0.08	0.26	0.02	0.03	0.05	0.01	0.72	1.06	
9	0.13	0.20	-0.03	0.05	-0.09	-0.02	0.52	0.40	
10	-0.51	0.36	-0.06	0.05	-0.46	-0.05	0.03	0.11	
11	-0.03	0.08	0.01	-0.00	0.04	-0.08	-0.02	0.01	
Species A_1 (continued)									
9	0.73								
10	0.04	16.16							
11	-0.02	-0.02	0.22						
Species A_2									
1	4.77								
2	0.01	0.33							
3	-0.03	-0.04	0.42						
4	-0.04	-0.07	-0.04	0.42					
5	0.00	-0.01	0.02	0.01	0.06				
6	0.01	-0.06	-0.01	-0.03	0.01	0.15			
Species B_1									
1	5.05								
2	-0.02	4.75							
3	-0.12	0.04	1.08						
4	-0.14	-0.05	0.12	0.40					
5	-0.24	-0.04	0.09	0.04	0.58				
6	0.05	-0.00	0.09	0.06	0.02	0.11			
7	-1.16	0.03	-0.02	-0.14	-0.12	0.03	15.32		
8	-0.07	0.00	-0.08	-0.03	-0.01	-0.04	-0.03	0.17	
Species B_2									
1	2.30								
2	-0.02	4.85							
3	-0.10	0.11	4.92						
4	-0.19	-0.00	-0.01	0.39					
5	-0.05	-0.04	0.03	-0.02	1.18				
6	0.13	0.02	0.02	-0.02	0.64	1.04			
7	0.09	-0.02	0.05	-0.03	0.46	0.37	0.65		
8	-0.21	-0.00	-0.01	0.02	-0.01	-0.02	-0.03	0.19	

atures of absolute zero and 298 K are given in Table 2. The table includes the calculated interatomic separations (in Å), which implicitly give information about the structural parameters applied in the present analysis. The corresponding calculations for $(CD_3)_2C(CN)_2$ revealed no substantial secondary isotope effects on the mean amplitudes ($<0.0003_2$ Å at 298 K). It seems therefore unnecessary to report the complete list of the mean amplitudes for

Table 2. Mean amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K) for 2,2-dicyanopropane; Å units.

Distance type	(Equil. dist.)	Atom pair	$u(0)$	$u(298)$	$K(0)$	$K(298)$
$C_1 - H_1^\circ$	(1.090)	3-6	0.0780	0.0780	0.0212	0.0289
$C_1 - H_1$	(1.090)	3-8	0.0780	0.0780	0.0215	0.0300
$C_1 - C_2$	(1.540)	3-5	0.0548	0.0573	0.0024	0.0037
$C_2 - C_2'$	(1.470)	1-5	0.0447	0.0456	0.0029	0.0040
$C_2 \equiv N$	(1.170)	1-12	0.0353	0.0354	0.0073	0.0138
$C_1 \cdots C_3$	(2.515)	3-4	0.0611	0.0646	0.0025	0.0048
$C_1 \cdots C_2'$	(2.458)	1-3	0.0686	0.0796	0.0021	0.0034
$C_2' \cdots C_2''$	(2.401)	1-2	0.0641	0.0766	0.0025	0.0036
$C_2 \cdots H_1^\circ$	(2.163)	5-6	0.1090	0.1106	0.0111	0.0167
$C_2 \cdots H_1$	(2.163)	5-8	0.1075	0.1090	0.0113	0.0169
$C_1 \cdots H_3^\circ$	(3.462)	3-7	0.1018	0.1035	0.0081	0.0132
$C_1 \cdots H_3'$	(2.741)	3-10	0.1390	0.1539	0.0086	0.0138
$C_2' \cdots H_1^\circ$	(2.698)	1-6	0.1483	0.1694	0.0081	0.0123
$C_2' \cdots H_1'$	(2.698)	1-8	0.1458	0.1663	0.0082	0.0123
$C_2' \cdots H_1''$	(3.399)	1-9	0.1016	0.1058	0.0077	0.0115
$C_1 \cdots N$	(3.472)	3-12	0.0760	0.1000	0.0015	0.0033
$C_2 \cdots N$	(2.640)	5-12	0.0499	0.0512	0.0025	0.0058
$C_2' \cdots N'$	(3.423)	1-13	0.0760	0.1044	0.0016	0.0033
$H_1 \cdots H_1^\circ$	(1.780)	6-8	0.1290	0.1292	0.0285	0.0429
$H_1 \cdots H_1'$	(1.780)	8-9	0.1283	0.1285	0.0293	0.0448
$H_1^\circ \cdots H_3^\circ$	(4.295)	6-7	0.1395	0.1406	0.0119	0.0201
$H_1 \cdots H_3^\circ$	(3.737)	6-10	0.1557	0.1642	0.0120	0.0185
$H_1 \cdots H_3'$	(2.515)	8-10	0.1953	0.2132	0.0166	0.0271
$H_1 \cdots H_3''$	(3.081)	8-11	0.2139	0.2632	0.0115	0.0164
$H_1^\circ \cdots N$	(3.527)	6-12	0.1669	0.2079	0.0056	0.0090
$H_1 \cdots N$	(3.527)	8-12	0.1647	0.2036	0.0055	0.0087
$H_1 \cdots N'$	(4.485)	8-13	0.1034	0.1152	0.0056	0.0090
$N \cdots N'$	(4.311)	12-13	0.0932	0.1506	0.0009	0.0016

Table 3. Mean amplitudes of vibration (u in Å units) for the distances in 2,2-dicyanopropane- d_6 which involve deuterium.

Distance type	(Equil. dist.)	Atom pair	$u(0)$	$u(298)$
$C_1 - D_1^\circ$	(1.090)	3-6	0.0667	0.0668
$C_1 - D_1$	(1.090)	3-8	0.0668	0.0668
$C_2 \cdots D_1^\circ$	(2.163)	5-6	0.0943	0.0972
$C_2 \cdots D_1$	(2.163)	5-8	0.0930	0.0957
$C_1 \cdots D_3^\circ$	(3.462)	3-7	0.0894	0.0920
$C_1 \cdots D_3'$	(2.741)	3-10	0.1197	0.1412
$C_2' \cdots D_1^\circ$	(2.698)	1-6	0.1294	0.1576
$C_2' \cdots D_1'$	(2.698)	1-8	0.1270	0.1546
$C_2' \cdots D_1''$	(3.399)	1-9	0.0895	0.0948
$D_1 \cdots D_1^\circ$	(1.780)	6-8	0.1087	0.1096
$D_1 \cdots D_1'$	(1.780)	8-9	0.1082	0.1089
$D_1^\circ \cdots D_3^\circ$	(4.295)	6-7	0.1185	0.1210
$D_1 \cdots D_3^\circ$	(3.737)	6-10	0.1323	0.1456
$D_1 \cdots D_3'$	(2.515)	8-10	0.1654	0.1929
$D_1 \cdots D_3''$	(3.081)	8-11	0.1808	0.2480
$D_1^\circ \cdots N$	(3.527)	6-12	0.1458	0.1973
$D_1 \cdots N$	(3.527)	8-12	0.1437	0.1931
$D_1 \cdots N'$	(4.485)	8-13	0.0923	0.1059

the deuterated compound. Table 3 shows the calculated mean amplitudes only for the distances in $(\text{CD}_3)_2\text{C}(\text{CN})_2$ which involve a deuterium atom. Complete lists of mean amplitudes and K values also for this molecule are available on request to the authors.

2,2-DIFLUOROPROPANE

The vibrational spectra of 2,2-difluoropropane have been investigated by Crowder and Jackson.⁸ They recorded the gas and liquid infrared spectra along with the Raman spectrum of the solid. They also performed a normal coordinate analysis.

We have developed a harmonic force field for 2,2-difluoropropane, which is given in Table 4 in terms of the specified symmetry coordinates. An initial force field was constructed by transferring the force constants from propane² except for the C–F stretching, for which the value of 4.28₃ mdyn/Å was taken.⁸

Table 4. Symmetry force constants (mdyn/Å) for 2,2-difluoropropane.

Species A_1									
1	5.36								
2	0.87	4.50							
3	-0.00	-0.03	4.87						
4	0.06	0.01	0.09	4.94					
5	-0.49	0.30	-0.03	0.02	1.40				
6	0.56	0.93	-0.01	0.03	1.22	2.62			
7	0.06	0.08	-0.04	0.03	-0.01	0.07	1.29		
8	0.02	0.34	0.01	0.03	0.01	0.06	0.79	1.14	
9	0.17	0.30	-0.03	0.06	-0.04	0.06	0.50	0.43	0.68
Species A_2									
1	4.82								
2	0.01	0.48							
3	-0.04	-0.01	0.42						
4	-0.05	-0.03	-0.04	0.41					
5	0.00	-0.01	0.03	0.02	0.12				
Species B_1									
1	4.54								
2	-0.05	4.82							
3	0.81	0.02	0.44						
4	0.03	-0.03	-0.01	0.42					
5	-0.04	-0.02	-0.06	0.01	0.52				
6	0.05	-0.00	0.02	0.00	-0.00	0.084			
Species B_2									
1	3.61								
2	0.01	4.89							
3	-0.05	0.08	4.95						
4	0.21	0.01	-0.01	0.44					
5	0.04	-0.02	0.02	-0.01	1.31				
6	0.26	0.02	0.02	-0.01	0.68	1.08			
7	0.25	0.01	0.03	-0.03	0.59	0.40	0.85		

The final force constants (Table 4) are adjusted so as to fit exactly the assignment of experimental frequencies from Ref. 8. In this assignment the lowest frequency of species B_1 (designated b_2 in Ref. 8) is unobserved. Crowder *et al.*⁸ have calculated the value 317 cm^{-1} . We preferred to use 242.1 cm^{-1} taken from a far-infrared investigation of Moeller *et al.*,⁷ who have reported the torsional frequencies of $\sim 232\text{ cm}^{-1}$ and 242.1 cm^{-1} , but pointed out that these observations are uncertain because of a complicated pattern.

The developed force field (Table 4) was used to calculate the mean amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K). The results are given in Table 5.

Table 5. Mean amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K) for 2,2-difluoropropane; Å units.

Distance type	(Equil. dist.)	Atom pair	$u(0)$	$u(298)$	$K(0)$	$K(298)$
$C_1-H_1^\circ$	(1.091)	3-6	0.0779	0.0779	0.0190	0.0241
C_1-H_1	(1.091)	3-8	0.0779	0.0779	0.0213	0.0291
C_2-F	(1.360)	1-5	0.0489	0.0502	0.0024	0.0030
C_1-C_2	(1.526)	3-5	0.0519	0.0526	0.0022	0.0027
$C_1\dots C_2$	(2.536)	3-4	0.0653	0.0714	0.0011	0.0013
$C_2\dots H_1^\circ$	(2.173)	5-6	0.1054	0.1060	0.0095	0.0123
$C_2\dots H_1$	(2.173)	5-8	0.1053	0.1061	0.0112	0.0160
$C_1\dots H_2^\circ$	(3.486)	3-7	0.1023	0.1049	0.0058	0.0077
$C_1\dots H_2$	(2.801)	3-10	0.1384	0.1513	0.0071	0.0101
$C_1\dots F$	(2.348)	1-3	0.0615	0.0632	0.0011	0.0015
$H_1\dots H_1^\circ$	(1.762)	6-8	0.1282	0.1286	0.0268	0.0386
$H_1\dots H_1'$	(1.761)	8-9	0.1293	0.1294	0.0291	0.0429
$H_1^\circ\dots H_2^\circ$	(4.324)	6-7	0.1408	0.1420	0.0079	0.0101
$H_1\dots H_2^\circ$	(3.802)	6-10	0.1561	0.1661	0.0101	0.0143
$H_1\dots H_2$	(2.625)	8-10	0.2029	0.2261	0.0128	0.0168
$H_1\dots H_2'$	(3.161)	8-11	0.2014	0.2279	0.0109	0.0155
$F\dots F'$	(2.221)	1-2	0.0619	0.0715	0.0011	0.0016
$H_1^\circ\dots F$	(2.631)	1-6	0.1365	0.1488	0.0067	0.0090
$H_1\dots F$	(2.638)	1-8	0.1446	0.1667	0.0073	0.0103
$H_1\dots F'$	(3.297)	1-9	0.0986	0.1007	0.0066	0.0092

2,2-DIIODOPROPANE

The available experimental data of vibrational frequencies for 2,2-diiodopropane are rather incomplete. The spectroscopic measurements are very difficult in this case because of the light-sensitivity of the compound. Tobin¹³ has proposed tentative vibrational assignments for 2,2-dichloro-, 2,2-dibromo-, and 2,2-diiodopropane on the basis of literature data. For the iodine compound he utilized the old and incomplete Raman data from Kahovec and Wagner.¹⁴

We have calculated the vibrational frequencies for 2,2-diiodopropane in the following way. The equilibrium C-I distance was assumed to be 2.106 Å ; otherwise the structural parameters were adopted from propane. All force constants were transferred from 2,2-dibromopropane² except those of C-I stretchings, which were assumed to be $F_{11}(A_1) = 2.1\text{ mdyn/Å}$ and $F_{11}(B_1) =$

1.8 mdyn/Å. The calculated frequencies are: (A_1) 3010, 2939, 1444, 1393, 1146, 900, 487, 279, and 126; (A_2) 2908, 1430, 1189, 407, and 253; (B_1) 2895, 1464, 1058, 518, 302, and 184; (B_2) 2979, 2938, 1456, 1382, 1111, 952, and 284; all values in cm^{-1} . These frequencies are roughly comparable to those of Tobin's¹³ assignment except for the low frequencies of species A_2 . We believe that the present assignment as a whole is the more reliable one.

The mean amplitudes of vibration were also calculated for 2,2-diiodopropane. They are naturally not so reliable because of the lack of complete

Table 6. Mean amplitudes of vibration (u in Å units) at 298 K for the distances in 2,2-diiodopropane which involve iodine.

Distance type	Atom pair	$u(298)$
C_2-I	1-5	0.060
$C_1 \cdots I$	1-3	0.076
$I \cdots I'$	1-2	0.083
$H_1^o \cdots I$	1-6	0.178
$H_1 \cdots I$	1-8	0.210
$H_1 \cdots I'$	1-9	0.108

experimental spectral data. We therefore only give the results at 298 K for some selected distances. Table 6 shows the mean amplitudes for those distances which involve an iodine atom. The values of $u(298)$ for the C-I and I...I distances in 2,2-diiodopropane (see Table 6) are comparable with the corresponding ones in Cl_4 , viz.^{5,15} 0.0628 Å and 0.0850 Å, respectively.

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