This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 23 February 2013, At: 06:54
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Infrared and Raman Spectra and Polymorphism in Crystal n-Butane

M. L. Cangeloni [a] & V. Schettino [a]

[a] Istituto di Chimica Fisica, Università di Firenze, Via G. Capponi, 9-50121, Firenze, Italy

Version of record first published: 29 Aug 2007.

To cite this article: M. L. Cangeloni & V. Schettino (1975): Infrared and Raman Spectra and Polymorphism in Crystal n-Butane, Molecular Crystals and Liquid Crystals, 31:3-4, 219-231

To link to this article: http://dx.doi.org/10.1080/15421407508082874

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1975, Vol. 31, pp. 219–231
© Gordon and Breach Science Publishers, Ltd.
Printed in Holland

Downloaded by [Tomsk State University of Control Systems and Radio] at 06:54 23 February 2013

Infrared and Raman Spectra and Polymorphism in Crystal *n*-Butane†

M. L. CANGELONI AND V. SCHETTINO

Istituto di Chimica Fisica, Università di Firenze, Via G. Capponi 9—50121 Firenze—Italy

(*Received May 16, 1975*)

The infrared and Raman spectra of crystal *n*-butane are reported. Evidence has been found that *n*-butane exist in three crystal forms having disordered (form I), monoclinic (form II) and triclinic (form III) structure. The packing in the triclinic low temperature form III has been studied by using atom–atom potentials. The structure obtained satisfactorily reproduces the Raman lattice frequencies.

1 INTRODUCTION

The crystal structure and polymorphism in *n*-paraffins has been the object of considerable attention.[1–3] In the even paraffins series it has been found that the structure of the low temperature form is in most cases triclinic (with one molecule per cell) or monoclinic (with two molecules per cell) depending on the chain length and sample purity. For several even paraffins at high temperatures a transition to a disordered form has been observed to take place with the onset of free rotation around the long molecular axis.

No detailed information is available on the structure of crystal *n*-butane which, as a lower member of the series, may show peculiarities due to the enhanced influence of the methyl groups. In the present paper the results of an infrared and Raman study of crystal *n*-butane are reported. It will be shown that *n*-butane can exist in three crystal forms having triclinic (form III), monoclinic (form II) or disordered (form I) structure. The discussion will particularly focus on the low temperature form III: starting from the spectroscopic information an attempt has been made to calculate the crystal structure by minimizing the crystal energy using a pairwise interaction

---

† Supported by the Italian Consiglio Nazionale delle Ricerche.

potential.[4] The calculated packing is compared with that of other hydrocarbons of the series.[5–7] The calculated structure satisfactorily reproduces the Raman lattice frequencies.

2 EXPERIMENTAL

The *n*-butane used for this research was a cromatographically pure sample obtained from Carlo Erba (Italy).

The infrared spectra between 4000 and 200 cm^{-1} were taken on a Perkin Elmer model 225 spectrophotometer with an average spectral slit width of 1 cm^{-1}. A conventional low temperature cell was used with CsI windows and the temperature was measured with a copper constantane thermocouple held in contact with the sample by an indium gasket. The Raman spectra were taken on a Cary 81 spectrometer equipped with an Argon ion laser source using the 4880 Å exciting line. The low temperature Raman cell designed for right-angle scattering geometry has been described by Castellucci.[8]

3 RESULTS

The most significant parts of the infrared and Raman spectra of crystalline *n*-butane are shown in Figures 1–4 and the results are summarized in Tables I and II.

Vapor deposition of *n*-butane on surfaces cooled at 77°K results in an admixture of two crystal forms with relative abundance depending on the rate of deposition. By annealing at 85–90°K a rapid conversion to a pure crystal form occurs which is stable at the lowest temperatures on further cooling (form III). When heated at about 110°K form III converts to a new crystal form (form I). The transition III → I is reversible and occurs at the same temperature as the transition observed in the heat capacity curve.[9] When cooled rapidly to 77°K form I transforms to a metastable form II, which by annealing eventually transforms again to form III. The original vapor deposited samples contain an admixture of forms II and III. The observation in the infrared and Raman experiments coincide; because of insufficient temperature control in the Raman cell it has not been possible to register the Raman spectrum of form I in full.

4 DISCUSSION

4.1 Assignment

The vibrational assignment of *n*-butane has been discussed in detail by Snyder and Schachtschneider[10,11] with the help of a normal frequencies

Downloaded by [Tomsk State University of Control Systems and Radio] at 06:54 23 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 06:54 23 February 2013

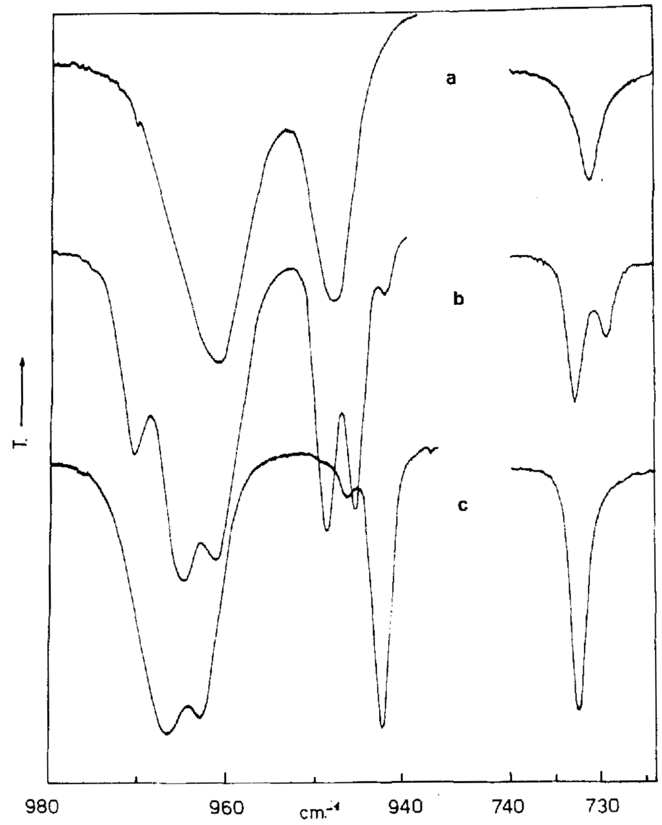

FIGURE 1 Infrared spectrum of crystal *n*-butane.
a: form I at −165°C; b: form II at −196°C; c: form III at −196°C.

calculation. Only two remarks are necessary: a) various fundamentals have not been considered in previous assignments, b) the agreement between calculated and observed frequencies is generally good except for the low frequency torsional motions. Concerning point a) all the missing fundamentals have been observed in the present study except one, ν_{26}, which falls outside the frequency range of our infrared instrument. This fundamental has however been observed by neutron scattering experiments.[12] The poor fit for the low frequency fundamentals may be due to inadequacy of the torsional force constants used by Snyder.[11] In the case of *n*-hexane crystal Brunel and Dows[13] ascribed the poor fit for the *g* modes to coupling with the lattice librational modes. We observe, however, that in *n*-hexane there is disagreement also for the infrared torsional frequencies which do not couple with the lattice modes. In addition in the Raman spectrum of liquid

Downloaded by [Tomsk State University of Control Systems and Radio] at 06:54 23 February 2013

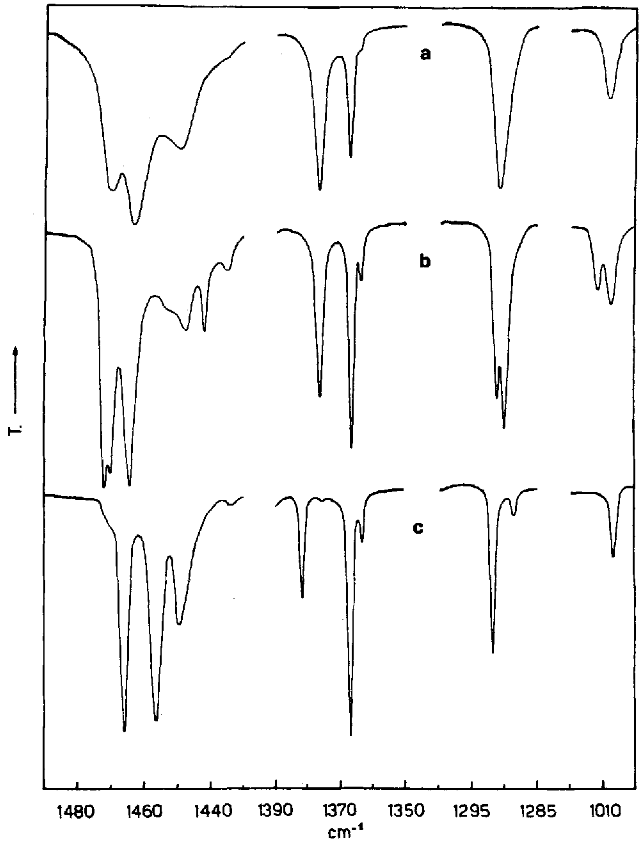

FIGURE 2 Infrared spectrum of crystal *n*-butane.
a: form I at −165°C; b: form II at −196°C; c: form III at −196°C.

n-hexane the only low frequency mode which is observed at room temperature ($\bar{\nu}_{\omega}^{0}$ of ref. 13) occurs at the same frequency (312 cm^{-1}) as in the crystal. It seems therefore that the disagreement should mainly involve the inadequacy of the force constants. We have recalculated the normal frequencies of *n*-butane in the trans conformation using a more realistic molecular structure than that used by Snyder. By using the results of the x-ray diffraction of *n*-hexane,[5] the bond parameters have been chosen as: C—H = 1.08 Å; C—C (central bond) = 1.53 Å; C—C (side bond) = 1.525 Å; $\widehat{\mathrm{CCC}} = 114°$; $\widehat{\mathrm{HCH}} = 111°$; $\widehat{\mathrm{HCC}} = 108°$. With a different geometry the calculated frequencies differ from those of Snyder and Schachtschneider[10,11] but the fit is promptly improved by refining the force field. The new values of the torsional force constants around the central and side CC bonds are 0.054

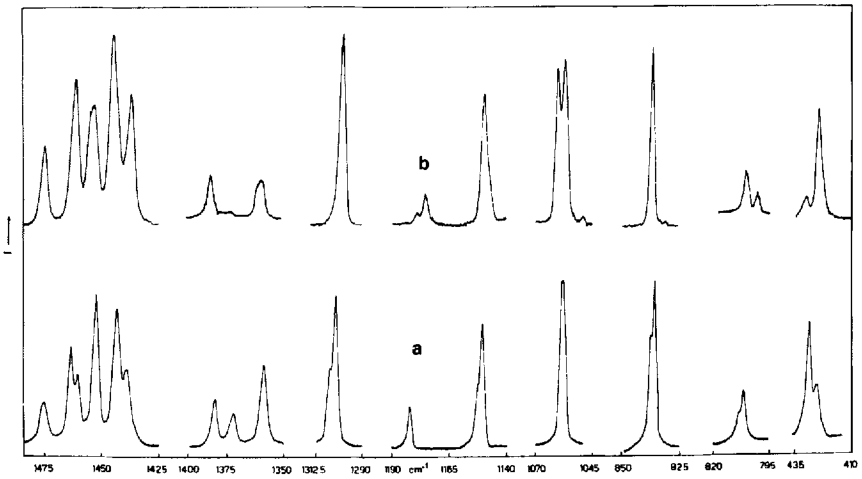

FIGURE 3 Raman spectrum of crystal *n*-butane at −196°C. a: form II; b: form III.

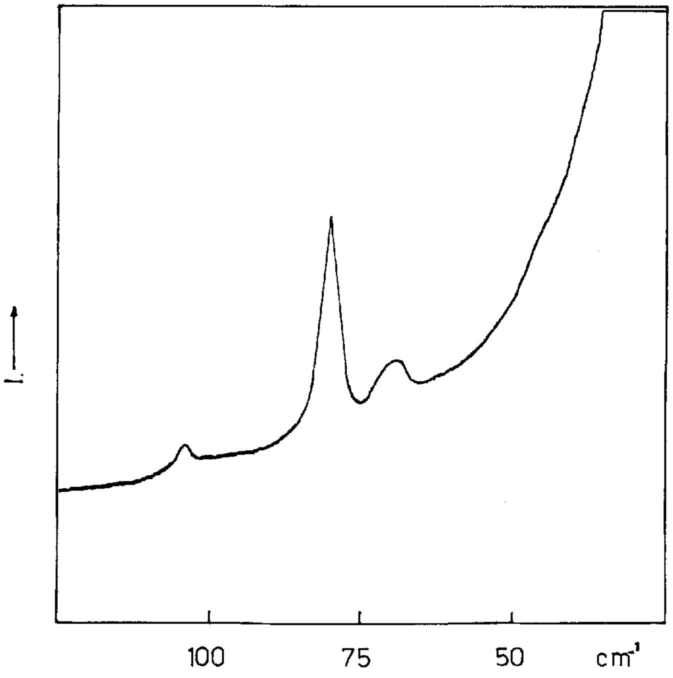

FIGURE 4 Raman lattice modes of form III of crystal *n*-butane at −196°C.

Downloaded by [Tomsk State University of Control Systems and Radio] at 06:54 23 February 2013

TABLE I

Infrared spectrum of crystal *n*-butane.

Form	I[a]	Form	II[b]	Form	III[b]	Assignment
				155[c]		$\nu_{26}(A_u)$
				233	vw	$\nu_{25}(A_u)$
				266.5	vw	$\nu_{36}(B_u)$
731	s	729 733	s s	732.5	s	$\nu_{24}(A_u)$
948	m	945 949	m m	943	m	$\nu_{23}(A_u)$
961	m	961 965	m m	963	m	$\nu_{35}(B_u)$
		970	m	966	m	$\nu_{17} + \nu_{26}$
		994	vw	995	vw	$\nu_{10} + \nu_{26}$
1009	vw	1008.5 1011	vw vw	1008	vw	$\nu_{34}(B_u)$
				1257	vw	$\nu_{22}(A_u)$
1290.5	w	1290 1291	w w	1291.7	w	$\nu_{33}(B_u)$
		1363	w	1363	w	$\nu_{11} + \nu_{23}$
1367.5	m	1367	s	1367	s	$\nu_{32}(B_u)$
1376.5	s	1376	s	1381	m	$\nu_{8} + \nu_{25}$
		1436	vw	1436	vw	$\nu_{16} + \nu_{36}$
1449	s	1442 1448	m m	1449	m	$\nu_{21}(A_u)$
1463	s	1464.5 1465.5	s sh	1456	s	$\nu_{31}(B_u)$
1470	s	1470 1472	s s	1466	s	$\nu_{30}(B_u)$
2859	s	2857 2860	s s	2859	s	$\nu_{29}(B_u)$
2872	vs	2872	vs	2872	vs	$\nu_{28}(B_u)$
				2912	s	
				2918	s	
2925	vs	2925	vs	2927	vs	$\nu_{20}(A_u)$
2935	s	2936	s			
				2941	s	
2956	vs	2956	vs	2953	vs	$\nu_{27}(B_u)$
2965	vs	2964	vs	2965	vs	$\nu_{19}(A_u)$

Frequencies in cm^{-1}; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

[a] Measured at 110°K

[b] Measured at 77°K

[c] Observed by neutron diffraction

Downloaded by [Tomsk State University of Control Systems and Radio] at 06:54 23 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 06:54 23 February 2013

TABLE II

Raman spectrum of crystal *n*-butane.

Form	II	Form	III	Assignment
266	vw	265	vw	$\nu_{18}(B_g)$
426 429	m m	425	m	$\nu_{11}(A_g)$
		429	m	$\nu_{26} + \nu_{30}$
		801	vw	
806.5 808.5	vw vw	807	vw	$\nu_{17}(B_g)$
834 837	s s	837	s	$\nu_{10}(A_g)$
841	w			
1058	s	1056.5	s	$\nu_9(A_g)$
		1060	s	$\nu_{17} + \nu_{18}$
1151 1152.5	m m	1149	s	$\nu_8(A_g)$
1182	m	1175	m	$\nu_{16}(B_g)$
1302 1304	s m	1298	s	$\nu_{15}(B_g)$
1359	w	1359	w	$\nu_7(A_g)$
1372 1380	w w	1382	w	$\nu_6(A_g)$
1438.5	s	1437	s	
1443	s	1445	s	$\nu_5(A_g)$
1452	s	1455	s	$\nu_{14}(B_g)$
1460 1463	s s	1462	s	$\nu_4(A_g)$
1475	s	1475	s	$\nu_9 + \nu_{11}$
2853	s	2853	s	$\nu_3(A_g)$
2873	s	2872	s	$\nu_2(A_g)$
2893	s	2896	s	$\nu_{13}(B_g)$
2910	m	2908	m	
2931	m	2832	m	
2945	m	2951	m	$\nu_{12}(B_g)$
2957	m	2957.5	vw	
2963	s	2963	s	$\nu_1(A_g)$

Frequencies in cm^{-1} at 77°K; s, strong; m, medium; w, weak; vw, very weak.

and 0.032 mdynÅ/$(rad)^2$, respectively. The other force constants also change slightly†.

4.2 Crystal spectra

The main feature of the infrared and Raman spectra, common to the three crystal forms, is that the mutual exclusion rule holds in the crystal. This

---

† The values of the refined force constants are available on request.

implies that in the solid state *n*-butane is in the trans conformation and retains the center of symmetry in the crystal. The other features of the three forms are considered separately.

Form I As has already been described the transition to form I occurs at 110°K. A transition at this temperature has also been observed in the heat capacity measurements[9] with a rather high entropy of transition (4.6 e.u.), showing that the high temperature form is disordered. This is confirmed in our infrared experiments since all the bands are rather broad and featureless. This is generally associated with a disordered crystal structure. It seems therefore that form I of *n*-butane closely resembles the hexagonal form of several other hydrocarbons in which the molecules rotate freely around the long axis. It is impossible however on the basis of the available data to establish if form I of *n*-butane is also hexagonal. In fact the crystal of 1-2-dichloroethane, which has a molecular shape very similar to that of *n*-butane, also exists in a high temperature disordered form in which the molecules rotate around the Cl—Cl axis.[14] This form is monoclinic as is the low temperature form.[15]

Form II The infrared bands in this crystal form are doublets in all cases where there is no overlapping with combination tones and in the few cases where the splitting is too small to be observed. The same occurs in the Raman spectrum. The most likely correlation diagram that can explain these features is one between a C_i site group and a C_{2h} factor group. With this type of structure six Raman active lattice vibrations are expected. None has however been observed. This can be due to weakness of the bands and their broadness at the temperature of the experiment. In fact in crystal *n*-hexane and *n*-octane a considerable broadening of lattice modes with increasing temperature has been reported.[13]

In the monoclinic structure of longer chain *n*-paraffins the long molecular axes are all parallel and the plane of the carbon atom skeleton is parallel to the *c* axis. It seems unlikely that form II of *n*-butane has a similar structure in the light of the results of x-ray diffraction studies on like molecules 1-2-dichloroethane[15] and ethylenediammine.[16] These compounds can both exist in a C_{2h}^5 structure with molecules oriented with the long axes almost perpendicular to each other. In view of the similar shape of *n*-butane with these molecules close packing concepts tend rather to suggest that form II of *n*-butane may be isomorphous with these crystals.

Form III The infrared and Raman bands in form III are single apart from occurrence of nearby combination bands. In this respect the strong ν_9 fundamental in the Raman spectrum looks very anomalous since it is a

Downloaded by [Tomsk State University of Control Systems and Radio] at 06:54 23 February 2013

singlet in form II and a doublet in form III. The only combination occurring in this region is $\nu_{17} + \nu_{18}$. It is possible that this doublet in form III is actually a Fermi dyad which is not observed in form II because the combination tone does not quite coincide with the fundamental. The singlet structure of the infrared and Raman spectra can be explained assuming that the molecules are located on the centers of symmetry of a triclinic unit cell. With this type of structure with one molecule per unit cell three Raman active librations are expected; these have actually been observed in the Raman spectrum (see Figure 4). The intensity pattern closely paralles that in *n*-hexane and *n*-octane.[13] This crystal form should then closely resemble the triclinic form of longer chain *n*-paraffins.

4.3 Molecular packing in form III

Atom–atom potentials for hydrocarbon molecules have been fairly well established by Williams on the basis of various properties of these compounds.[17,18] These atom–atom potentials have been shown capable of reproducing satisfactorily the x-ray structure of *n*-hexane and *n*-octane and their lattice frequencies.[13] Therefore it was thought interesting to use these parameters to calculate the structure of form III of *n*-butane corresponding to the minimum of the crystal energy as the sum of pairwise interactions.

The method and program used has been described by Williams.[19] The molecular structure of *n*-butane is the same used in the normal frequencies calculation but assuming a C—H bond length of 1.02 Å. The atomic coordinates used are reported in Table III. For the choice of the initial trial structure it can be noted that the long spacing in the triclinic structure of the even paraffins varies regularly by 2.4 Å in successive members of the series, while the other lattice constants show slight random variations. Therefore the initial trial structure and molecular orientation were the same as those of *n*-hexane except for the shortening of the *c* axis. Using set VI of Williams parameters[18] reported in Table IV and a 6 Å interaction radius the crystals

TABLE III

Atomic coordinates of *n*-butane in the molecular principal axis system.

	X	Y	Z
C_1	0	−0.143	1.960
C_2	0	0.502	0.577
H_1^3	0	0.627	2.629
$H_1^1 - H_1^2$	±0.849	−0.706	2.007
$H_2^1 - H_2^2$	±0.846	1.067	0.498

Downloaded by [Tomsk State University of Control Systems and Radio] at 06:54 23 February 2013

TABLE IV

Potential parameters.

Contact	A (Kcal. mole^{-1})	B (Å^{-1})	C (Kcal. Å^6 mole^{-1})
H H	32,3	2630.0	3.74
H C	128.0	11000.0	3.67
C C	505.0	61900.0	3.60

energy is positive. By refining the lattice constants and the molecular orientation the energy rapidly becomes negative: during the initial refinement only the molecular orientation changes while the other lattice constants remain almost unchanged. By a further refinement the energy slowly converges toward a minimum with a readjustment of all the lattice constants. As has been discussed by Williams[19] the equilibrium structure obtained with this method depends on the initial trial structure. This has indeed been observed in the present case, but no systematic study has been made of the dependence of the final on the initial structure, particularly because of the uncertainty of the intramolecular parameters. In all attempts made the final structures obtained are very similar. A projection of the structure corresponding to the lowest minimum obtained is shown in Figure 5 and the crystal parameters and molecular orientation are reported in Table V. The sublimation energy is calculated as 7.4 Kcal/mole and compares well with the experimental value; the agreement is similar to that found in *n*-hexane and *n*-octane.[13] The calculated density of crystal *n*-butane (0.86 g/cm^3) also compares well with that of *n*-hexane and *n*-octane.[5,6] The structure of *n*-butane, like that of homologous hydrocarbons,[5,6] consists of chains of molecules but the long axes of the *n*-butane molecules are not quite as parallel as in the other paraffins, as can be seen from the values of the direction cosines of Table V. In addition in *n*-butane one chain of molecules is shifted with respect to the neighbors in such a way that they interlock differently than in other hydrocarbons. These differences in packing may

TABLE V

Crystal parameters and molecular orientation of *n*-butane.

a (Å)	4.182	
b (Å)	5.402	$R = \begin{pmatrix} 0.82843 & 0.33164 & 0.45029 \\ -0.55409 & 0.5699 & 0.60449 \\ -0.05422 & -0.75027 & 0.65912 \end{pmatrix}$
c (Å)	5.055	
α (degrees)	94.06	
β (degrees)	89.49	
γ (degrees)	103.39	

Downloaded by [Tomsk State University of Control Systems and Radio] at 06:54 23 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 06:54 23 February 2013

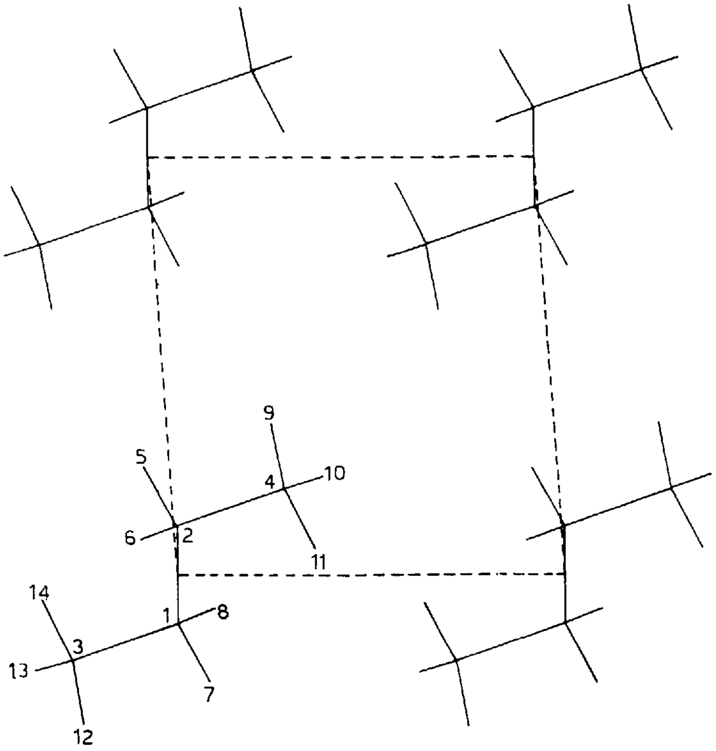

FIGURE 5 Molecular packing of *n*-butane in crystal form III.

well be ascribed to the importance of the methyl groups in determining the preferred mutual orientation of the molecules.

4.4 Calculation of the lattice frequencies of form III of *n*-butane

Having calculated the crystal structure of *n*-butane it is interesting to use this structure to calculate the lattice frequencies and to compare them with the observed values. As a matter of fact the lattice frequencies should be rather sensitive to the crystal structure and therefore this constitutes a check for the results of the packing calculation. The method used to obtain the lattice frequencies has been discussed in detail by Taddei *et al.*[22] The crystal frequencies are obtained by diagonalization of the dynamical equation:

$$|F_{\mu l}^{\nu m}(k) - (\lambda(k) - \lambda_l^0)\delta_{\mu\nu}\delta_{lm}| = 0$$

where μ and ν label different molecules and l and m the molecular normal coordinates, including Eckart translational and rotational coordinates.

The way to obtain the expression for the elements of the dynamical matrix in terms of an atom–atom potential has recently been rediscussed by Neto *et al.*[23] who have shown that previous expressions[22] were incomplete and an additional term should be included to take full account of the curvilinear nature of the librational coordinates.

Lattice frequencies have been calculated in the rigid body approximation. For sake of comparison the calculation of the lattice frequencies of *n*-hexane has been repeated since previous calculations by Brunel and Dows[13] were performed with the incomplete expression of the elements of the dynamical matrix given in ref. 22. The results are given in Table VI and compared with experiments. The *n*-butane frequencies have been corrected to 20°K assuming that their temperature dependence is parallel to that observed in *n*-hexane.[13] The fit in *n*-butane is excellent and comparable to that found in *n*-hexane.[13] This agreement may be a good piece of evidence in favor of the correctness of the packing calculation.

TABLE VI

Observed and calculated frequencies in the rigid body approximation of *n*-butane and *n*-hexane.

Butane			Hexane		
$\nu_{obs.}$ (78°K)	$\nu_{obs.}$ (20°K)	$\nu_{calc.}$	$\nu_{obs.}$ (80°K)	$\nu_{obs.}$ (20°K)	$\nu_{calc.}$
104	110	115	82	87	90
80	84	88	71	74	68
68	63	71	59	53	60

References

1. A. Müller, *Proc. Roy. Soc.* (London) **A127**, 417 (1930); **A138**, 514 (1932).
2. S. M. Ohlberg, *J. Phys. Chem.* **63**, 248 (1959).
3. E. F. Westrum, Jr. and J. P. McCullough, in *Physics and Chemistry of the Organic Solid State*, Ed. Fox, Labes and Weissberger, vol. 1, 1963 Interscience.
4. D. A. Dows, in *Proceeding of the Enrico Fermi Internation Summer School* on Lattice Dynamics and Intermolecular Forces, Varenna 1972.
5. N. Norman and H. Mathisen, *Acta Chem. Scand.* **15**, 1755 (1961).
6. N. Norman and H. Mathisen, *Acta Chem. Scand.* **15**, 1747 (1961).
7. H. Mathisen, N. Norman, and B. F. Pedersen, *Acta Chem. Scand.* **21**, 127 (1967).
8. E. Castellucci, Spectrochim. *Acta 29* A, 1217 (1973).
9. J. G. Aston and G. H. Messely, *J. Am. Chem. Soc.* **62**, 1917 (1940).
10. R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta* **19**, 85 (1963); **19**, 117 (1963).
11. R. G. Snyder, *J. Chem. Phys.* **47**, 1316 (1967).
12. K. A. Strong quoted in K. W. Logan, H. R. Damer and J. D. Ganet, *J. Chem. Phys.* **59**, 2305 (1973).

Downloaded by [Tomsk State University of Control Systems and Radio] at 06:54 23 February 2013

13. L. C. Brunel and D. A. Dows, *Spectrochim. Acta* 30 A, 929 (1974).
14. M. E. Milberg and W. N. Lipscomb, *Acta Cryst.* **4**, 369 (1951).
15. T. B. Reed and W. N. Lipscomb, *Acta Cryst.* **6**, 45 (1953).
16. S. Jamet-Deleroix and H. Gillet-Pandrand C. R. Acad. Sc. Paris 274 C, 771 (1972).
17. D. E. Williams, *J. Chem. Phys.* **45**, 3770 (1965).
18. D. E. Williams, *J. Chem. Phys.* **47**, 4680 (1967).
19. D. E. Williams, *Acta Cryst.* A 25, 464 (1969); USAEC Report IS–1042 (1964).
20. D. E. Williams, *J. Chem. Phys.* **43**, 4424 (1963).
21. A. Bondi, *J. Chem. and Engineering data* **8**, 371 (1963).
22. G. Taddei, H. Bonadeo, M. P. Marzocchi, and S. Califano, *J. Chem. Phys.* **58**, 966 (1973).
23. N. Neto, G. Taddei, S. Califano, and S. H. Walmsley, to be published.

Downloaded by [Tomsk State University of Control Systems and Radio] at 06:54 23 February 2013