Nous tenons à remercier M J. P. Astier pour l'enregistrement des intensités diffractées qui a été effectué au Centre de Recherche sur les Mécanismes de la Croissance Cristalline à Marseille.

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Study of the Solid Modifications of Ethane by Energy Calculations. Evaluation of the Fast-Summation Technique in *WMIN*

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Abstract

Potential-energy calculations have shown that the crystal structure reported by Marck & Poland [Z. Kristallogr. (1925), 62, 103–112] is not favourable for ethane. For the phase stable between 89·726 and 89·834 K at very low pressures, a disordered structure analogous to that of the ordered monoclinic phase stable below 89·726 K is proposed.

Introduction

For ethane three solid modifications are known at very low pressures: a plastic cubic modification (I) stable directly below the melting point of 90·352 (1) K, a phase (II) stable between 89·834 (1) and 89·726 (1) K, and a monoclinic phase (III) stable below 89·726 (1) K. The crystal structures of (I) and (III) have been reported by van Nes & Vos (1978). The existence of phase (II) was found from NMR spectra (Schutte, 1979) and from calorimetric measurements (Pavese, 1978). Attempts to identify this phase in our laboratory by X-ray diffraction have not been successful so far. The transition energy is 90 (10) J mol^{-1} for the transition (III)→(II) and 2050 (20) J mol^{-1} for (II)→(I) (Pavese, 1978).

Until the structure determinations by van Nes & Vos (1978) the hexagonal structure proposed by Marck & Poland (1925) for ethane had been used as a basis for the explanation of the PMR spectra (Givens & McCormick, 1977, and references therein). The recent structure determinations have shown, however, that this hexagonal structure is not correct for phases (I) and (III). In the present paper results of potential-energy calculations have been used to check whether the Marck & Poland structure may be favourable for another phase of ethane and the possibility that Marck & Poland may have crystallized phase (II) is discussed.

Potential function, computer program

Intermolecular interactions have been calculated for rigid molecules with Buckingham-type atom–atom potential functions (Hirschfelder, Curtiss & Bird, 1954) and Williams's (1970) parameter set C. The computer program used is a slightly modified version of *WMIN* (Busing, 1972). Convergence acceleration (Williams, 1971) has been applied with a convergence constant of

0·26, a reciprocal-space summation limit of 0·7 Å⁻¹ and, unless stated otherwise, a direct-space summation limit of 7·0 Å.

The influence of convergence acceleration and of the fast-summation technique, included as an option in *WMIN*, was checked in a series of calculations on the accurately determined monoclinic ethane structure. Results are given in Table 1. Direct-space summation limits (L) of 5·0 and 7·0 Å were applied. Energies were computed for different rotations φ of the ethane molecules around their C—C axes, but only values at $\varphi = 0$ (the position reported by van Nes & Vos, 1978), 120 and $-120°$ are listed for the present purpose. During the rotation of the molecules the symmetry $P2_1/n$ of the crystal is retained. Comparison of the $\varphi = 0°$ values for the different series shows that at $L = 7·0$ Å convergence is reached, when convergence acceleration is used. This has been confirmed by an additional summation with $L = 8·0$ Å. The $\varphi = 0°$ values at $L = 5·0$ Å show that, for this limit, use of convergence acceleration gives an appreciable improvement of the energy. Series 1 and 3 have quite large differences between the energies calculated at $\varphi = 0$, 120 and $-120°$, despite the fact that the molecular symmetry deviates very little from threefold inversion symmetry (3). The differences are due to the fast-summation technique. At the start of the calculation, in the present case at $\varphi = 0°$, the fast-summation option stores all interatomic vectors r_{ij} with $|r_{ij}| \leq L$, and uses these vectors for the determination of the inter-molecular energy. After rotation of the molecules the same set of vectors is used, their lengths and the energy

being found from the new atomic positions. However, no new vectors r_{nm} with $|r_{nm}| \leq L$ are added and vectors r_{ij} with $|r_{ij}| > L$ are not deleted. For $L = 5·0$ Å and $\varphi = 120°$ the left-hand side of Fig. 1 shows the number of vectors with $|r_{nm}| \leq 5·0$ Å omitted from the summation (part A) and the number of vectors with $|r_{ij}| > 5·0$ Å included in the summation (part B). It is seen that as many as seven vectors with length less than 3·0 Å are omitted. The shortest vector omitted (2·554 Å) is even shorter than the shortest (2·584 Å) included in the calculation for $\varphi = 120°$. On the other hand for $L = 7·0$ Å (right-hand side of Fig. 1) only one
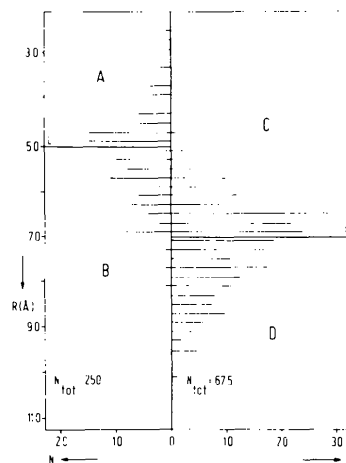

Fig. 1. Number N of interatomic vectors with length between R and $R + 0·2$ Å, omitted or retained by the fast-summation technique in *WMIN* for monoclinic ethane at 120°.

Table 1. *Potential-energy calculation on monoclinic ethane*

Number	Fast sum	Convergence acceleration	Limit L (Å)	φ (°)	vdW*	rep†	total
				-120	$-21·690$	$12·416$	$-9·274$
1	yes	no	5·0	0	$-25·284$	$15·809$	$-9·475$
				$+120$	$-21·578$	$13·002$	$-8·576$
				-120	$-25·280$	$15·800$	$-9·479$
2	no	no	5·0	0	$-25·284$	$15·809$	$-9·475$
				$+120$	$-25·271$	$15·784$	$-9·488$
				-120	$-25·447$	$12·416$	$-16·043$
3	yes	yes	5·0	0	$-30·597$	$15·809$	$-14·788$
				$+120$	$-28·526$	$13·002$	$-15·524$
				-120	$-30·597$	$15·800$	$-14·796$
4	no	yes	5·0	0	$-30·597$	$15·809$	$-14·788$
				$+120$	$-30·588$	$15·784$	$-14·801$
				-120	$-30·718$	$15·825$	$-14·897$
5	yes	yes	7·0	0	$-30·731$	$15·834$	$-14·897$
				$+120$	$-30·710$	$15·804$	$-14·901$
				-120	$-30·731$	$15·825$	$-14·905$
6	no	yes	7·0	0	$-30·731$	$15·834$	$-14·897$
				$+120$	$-30·718$	$15·809$	$-14·914$

* Van der Waals attractive energy.
† Repulsive energy.

vector shorter than 5·0 Å is omitted at $\varphi = 120°$ (part C). Series 5 and 6 in Table 1 show that for $L = 7·0$ Å use of the fast-summation technique gives only negligibly small errors in the calculated energy. All further calculations were therefore carried out with $L = 7·0$ Å and the fast-summation technique plus convergence acceleration. In spite of the relatively large value to be taken for L, fast summation with $L = 7·0$ Å is still more than 10 times faster than slow summation (all vectors $< L$ identified each time) with $L = 5·0$ Å.

Energies of the different phases

Monoclinic structure

The energy of the experimental structure was calculated at $-14·897$ kJ mol^{-1}. A Newton–Raphson minimization of the molecular orientation with the positions of their centres, the unit-cell dimensions and the symmetry fixed, shifted the C atoms less than $2·5 \times 10^{-3}$ Å. The minimal energy is $-14·930$ kJ mol^{-1}.

Plastic cubic modification

The plastic cubic modification has orientational disorder of the two ethane molecules, at (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, in the unit cell. Predominant orientations of the molecules are along the body diagonals. For the potential-energy calculations staggered ethane molecules (symmetry $\bar{3}$) were taken with C—C = 1·532, C—H = 1·095 Å and C—C—H = 109·5°. Molecule (1) was placed with its centre at (000) with C—C along |111|. For molecule (2) two possibilities were considered: (A) molecule (2) at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ with C—C along |111|; (B) molecule (2) at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ with C—C along |1̄11|. Note that these structures do not obey the cubic symmetry of the average structure. During the energy minimization for both molecules independent rotations around three perpendicular axes were applied with further variables fixed. Starting from structure (A) a subsidiary minimum with a potential energy of $-4·64$ kJ mol^{-1} was reached. Starting from (B) a minimal potential energy of $-13·608$ kJ mol^{-1} was obtained.

According to the PMR spectra of Givens & McCormick (1977) the disorder in the cubic phase has a dynamic character. The minimal potential energy calculated above is thus a lower bound for the actual energy as not at all instants will neighbouring molecules have the most favourable orientations relative to each other. Furthermore, intramolecular deformations may occur during the large rotations of the molecules. The energy of the cubic phase is therefore given by $(-13·608 + \delta)$ kJ mol^{-1}. This does not include the usual thermal energy also encountered in ordered structures, which drops out when energy differences between the phases are considered.

The Marck & Poland (MP) structure

The MP structure is hexagonal. The C atom skeleton is shown schematically in Fig. 2(a) and the structure after insertion of H atoms in Fig. 3(a). [In Fig. 3(a) the origin of the unit cell is shifted by $-\frac{1}{3},+\frac{1}{3},-\frac{1}{4}$ in
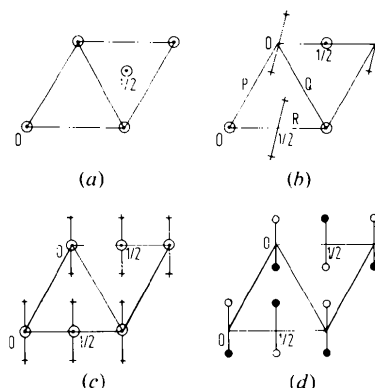
Fig. 2. C-atom skeletons of measured and proposed ethane structures; c (hex) is perpendicular to the plane of the drawing; heights of the molecular centres are indicated; + = C at same height as centre, ● – C above, ○ = C below centre and ⊙ = C—C perpendicular to drawing. (a) Hexagonal structure proposed by Marck & Poland (1925). (b) Monoclinic structure described in the hexagonal MP cell (periodicity not obeyed for molecular orientation). For relation with monoclinic cell see van Nes & Vos (1978). (c) Disordered orthorhombic structure directly derived from (b). (d) Ordered orthorhombic structure.
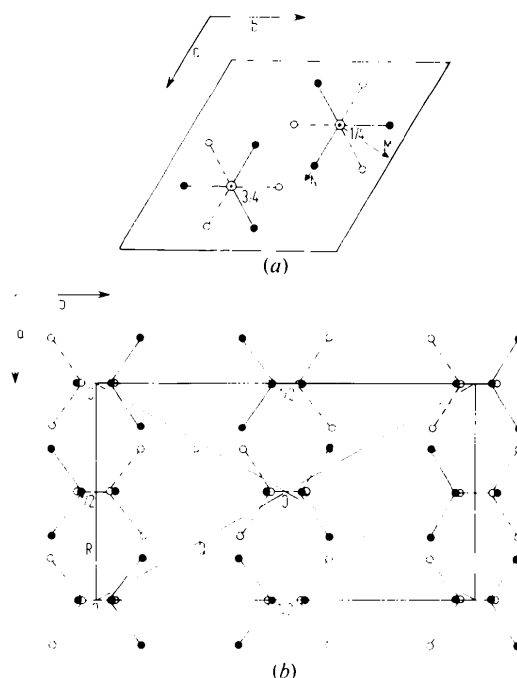
Fig. 3. Possible ethane structures. Heights of the molecular centres are indicated; ● = above centre, and ○ – below centre. (a) MP structure with H atoms placed such that the energy is minimal for rotation around C—C. (b) Ordered orthorhombic structure with MP periodicity, symmetry $Cmca$. Lines P, Q and R correspond to Fig. 2(b).

comparison with Fig. 2(a).] The ethane molecules were assumed to have symmetry $\bar{3}$ with C—C = 1·532, C—H = 1·095 Å and C—C—H = 111·5°. Energy minimization for rotation around C—C showed the structure of Fig. 3(a) to be in a local energy minimum with a potential energy as high as −2·794 kJ mol⁻¹. Further energy minima were detected by mapping the energy for varying rotations around C—C and around axes M and N perpendicular to C—C (Fig. 3a), and for varying values of the cell dimensions. Observed energy minima were located more accurately by the Newton–Raphson energy-minimization method. For four different local energy minima the structural param-eters (rotations relative to Fig. 3a) are given in Table 2.

Table 2 shows that MP-like structures with energies comparable to the monoclinic phase are obtained only for large changes in the cell dimensions. It must thus be concluded that an MP structure obeying the positions of the diffraction lines in the powder diagram is not favourable for ethane.

Alternative explanations of the MP powder diagram

Two structures were set up as possible explanations of the MP powder diagram.

(A) The disordered orthorhombic structure

As has been noted by van Nes & Vos (1978) the monoclinic structure of phase (III) is pseudohexagonal as far as the location of the molecular centres is concerned. Fig. 2(b), which gives a schematic picture of the monoclinic structure, shows that the structure has the periodicity of the MP cell for its molecular centres. The periodicity along P is not obeyed, however, for the molecular orientations, successive molecules along P having their C—C bonds almost perpendicular to each other. The periodicity of the MP cell may be intro-duced by assuming random disorder of all molecules over the two mutually perpendicular orientations of Fig. 2(b). After some further slight rotations the disordered orthorhombic structure of Fig. 2(c) (space

group $Fmmm$ for the C—C skeleton) is obtained. As discussed for the plastic cubic phase, the potential energy of this disordered structure is expected to be (slightly) higher than for the ordered monoclinic structure and is thus given by $(−14·930 + \delta^1)$ kJ mol⁻¹.

(B) The (ordered) orthorhombic structure

The MP periodicity can also be introduced in Fig. 2(b) by rotation of the molecules through 45° around R, alternating molecules in the P direction being rotated in the opposite sense. After some further small rotations the idealized orthorhombic structure of Fig. 2(d) is obtained (space group $Cmca$). The structure after inclusion of H atoms is given in Fig. 3(b). Energy minimization by rotation of the molecules around C—C and around axes M and N perpendicular to C—C showed the structure to be in a local energy minimum. The energy is as low as −17·520 kJ mol⁻¹.

For both structures (A) and (B) the calculated intensity variations show fair qualitative agreement with the MP powder data for the high-order reflections. For the low-order region $(\theta < 15°$ for Cu radiation) the estimated experimental intensities are relatively too weak. It cannot be excluded, however, that this is due to errors in the early powder data. For the monoclinic structure (III) the agreement with the MP powder diagram is appreciably worse.

A possible structure of phase (II)

In Table 3, column 2, the calculated energies of the structures (A) and (B) of the plastic cubic phase are given relative to the energy of the low-temperature monoclinic phase. In column 3 the transition enthalpies (Pavese, 1978) are given and in column 4 the densities of the different structures. As expected the value 1·334 kJ mol⁻¹ calculated for the energy difference between (I) and (III) is too small, but of the right order of magnitude. For the ordered orthorhombic structure the calculated energy is remarkably low. Therefore, such a

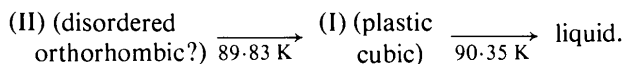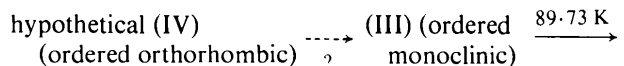Table 2. *Hypothetical MP-like structures with local energy minima*

ρ_c calculated density; SC = symmetry constraint during minimization; SO = symmetry after minimization; D +: cell dimensions varied; D —: dimensions not varied.

Number	SC	D	a (Å)	b (Å)	c (Å)	ρ_c (Mg m⁻³)	C–C (°)	M (°)	N (°)	SO	E (kJ mol⁻¹)
1	$P\bar{3}$	-	4·46	4·46	8·19	0·693	0·00			$P\bar{3}1c$	−2·794
2	$P\bar{1}$	-	4·46	4·46	8·19	0·693	0·00	0·00	32·72	$P\bar{1}$	−10·588
3	$P\bar{1}$	+	4·21	4·21*	9·71	0·669	0·00	0·00	0·00	$P\bar{3}1c$	−14·914
4	$P\bar{1}†$	+	4·21	4·21*	9·71	0·669	0·00			$P\bar{3}1c$	−14·914

* Constraint $b = a$.
† Independent rotation around and translation along C—C permitted, but translation found to be zero.

structure is not a possible candidate for phase (II), but might be stable at very low temperatures. The best hypothetical structure for (II) is the disordered orthorhombic structure, as in agreement with experiment its energy is expected to be (slightly) higher than for the ordered monoclinic phase. This hypothesis gives the following picture for the phase transitions in ethane at zero pressure:

hypothetical (IV)   (III) (ordered $\xrightarrow{89 \cdot 73 \text{ K}}$
(ordered orthorhombic) $\xrightarrow[?]{\text{----}}$ monoclinic)

(II) (disordered $\xrightarrow{89 \cdot 83 \text{ K}}$ (I) (plastic $\xrightarrow{90 \cdot 35 \text{ K}}$ liquid.
orthorhombic?)   cubic)

When (III) is heated, orientational disorder for the molecules sets in at 89·73 K which at an increase in temperature of only 0·1 K is followed by a much stronger (dynamical) orientational disorder. This qualitative picture agrees with NMR measurements (Schutte, 1979).

As far as its calculated powder pattern is concerned, it is not impossible that a phase (II) with the orthorhombic disordered structure corresponds to the MP powder diagram. The small stability region of this phase and the small transition energy to (III) do not make it very likely, however, that Marck & Poland have frozen-in this phase at zero pressure. Accidental crystallization of phase (II) is easier to achieve at higher pressures, as NMR data (Schutte, 1979) have shown that the stability region of (II) increases with

Table 3. *Calculated and observed data for experimental and proposed ethane structures*

	E_c (kJ mol^{-1})	H_{obs} (kJ mol^{-1})	ρ (Mg m^{-3})
Plastic cubic (I)	$1 \cdot 334 + \delta$	2·140	0·669
Disordered orthorhombic (A)	δ^1		0·693
Phase (II)		0·090	
Ordered monoclinic (III)	0	0	0·719
Ordered orthorhombic (B)	$-2 \cdot 590$		0·693

increasing pressure, but it is doubtful whether such pressures have been realized in Marck & Poland's sample.

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The Structure of Treptilaminum: an Anticholinergic Drug

By A. Perales, M. Martínez-Ripoll and J. Fayos

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Abstract

$C_{20}H_{28}NO^+ \cdot Cl^-$, $M_r = 333 \cdot 90$, monoclinic, $P2_1/c$, $a = 11 \cdot 267$ (2), $b = 31 \cdot 610$ (9), $c = 10 \cdot 803$ (1) Å, $\beta = 98 \cdot 71$ (1)°, $U = 3803 \cdot 1$ Å^3, $Z = 8$, $D_c = 1 \cdot 166$ Mg m^{-3}, $F(000) = 1440$. The final $R = 0 \cdot 087$ for 3956 reflections. The acetylcholine-like moiety adopts a conformation similar to that of acetylcholine in crystals of the chloride and bromide, as well as in other anticholinergic drugs. Both crystallographically independent molecules have the same bond lengths and angles, but their conformations have significant differences due to packing forces. The nortricycline moiety displays non-crystallographic $3m$ symmetry. Each molecule is involved in a N–H···Cl salt bridge.

Introduction

Treptilaminum, 2-[α-(tricyclo[2.2.1.0^{2,6}]hept-3-ylidene)benzyloxy]triethylamine, ASTA S5521, belongs to a class of synthetic drugs closely related to