

## Re-discovery and re-definition of dinite, $C_{20}H_{36}$ , a forgotten organic mineral from Garfagnana, northern Tuscany, Italy

LIVIA FRANZINI\*, MARCO PASERO\*\* and NATALE PERCHIAZZI\*\*\*

\* Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35,  
I-56126 Pisa, Italy

\*\* Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53,  
I-56126 Pisa, Italy

\*\*\* Museo di Storia Naturale e del Territorio, Università di Pisa, Via Roma 103,  
I-56011 Calci (PI), Italy

**Abstract :** The rare organic mineral dinite was found during the last century at Castelnuovo Garfagnana, Tuscany, Italy. After a chemical study, which indicated an erroneous chemical formula  $C_{18}H_{16}$ , it was stored in the Mineralogical Museum of the University of Pisa, where it was recently relocated. A new chemical analysis was carried out on dinite, and NMR, IR and mass spectra are presented here. The new data allows a re-definition of dinite as a distinct mineralogical species, with chemical formula  $C_{20}H_{36}$ . Single crystal X-ray diffraction work showed dinite to be orthorhombic, space group  $P2_12_12_1$ , with  $a = 12.356$ ,  $b = 12.762$ ,  $c = 11.427$  Å. Its crystal structure has been refined up to  $R = 0.068$ . Dinite is an alicyclic saturated hydrocarbon with three condensed cycles in the formula unit.

**Key-words :** dinite, 1-ethyl-1,5,5', 13-tetramethyl-perhydrophenanthrene, hydrocarbons.

### Introduction

Dinite is an organic mineral which was found within a lignite deposit in the Garfagnana valley, northern Tuscany, Italy. The name dinite was chosen by Prof. Meneghini in honour of Prof. Dini, who found the mineral. This naming of dinite was reported by Petri (1852), who first described the mineral and presented its chemical and physical data.

The first mention of this new mineral in a mineralogical treatise is found in Dana (1854). In that book, following a well-established rule, the name dinite is followed by the name of the person who gave the mineral its name, namely Meneghini, at that time Director of the Mineralogical Museum of the University of Pisa.

However, Meneghini did not publish anything on dinite ; the original description of the mineral was presented by Petri (1852), who was professor of Chemistry at the University of Pisa. As a matter of fact, after the quotation "DINITE *Meneghini*, *Gaz. Med. Italiana*" which appeared in Dana (1854), all the references to the original paper by Petri (1852) (e.g. Cocchi, 1856 ; Doelter & Leitmeier, 1931 ; Hintze, 1933) are erroneously attributed to Meneghini, and the role of G. Petri as the first scientist who studied dinite has been ignored.

After a short note by Ciusa & Galizzi (1921), no further authors published work on dinite, and now it merely represents one of the several names introduced in the mineralogical literature to denote a poorly defined mineral ; it

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surveys only in the more comprehensive compilations of minerals (*e.g.* Strunz, 1978).

### Re-discovery of dinite

One of us (NP), curator of the mineralogical collections of the Museum of Natural History at the University of Pisa, during classification of the older specimens, found a crystalline mass within a small glass container labelled: "Dinite  $C_{18}H_{16}$  Castelnuovo Garfagnana". The catalogue *no.* 1891, which is reported on the label, was attributed by Prof. A. D'Achiardi, director of the Mineralogical Museum in the years 1874-1910. D'Achiardi (1873) describes dinite as follows: "Dinite was named in honour of Prof. Dini and comes from Castelnuovo Garfagnana; it was firstly brought to our attention by Prof. Meneghini. It has an "icy" appearance and is transparent and very brittle. It is insoluble in alcohol, but is very soluble in carbon disulphide or in ether, in which large crystals are deposited. It fuses with the warmth of the hand. It is found in the bituminous fossil woods occurring under the alluvial deposits of Garfagnana, along the Serchio valley". Such a description is all but identical to that offered by Petri (1852), if exception is made of the locality at which dinite was claimed to have been found; Garfagnana is given by D'Achiardi (1873), and Lunigiana by Petri (1852). We think that the former locality is the correct one, *i.e.* Castelnuovo Garfagnana, which is the one indicated by the Italian authors D'Achiardi (1873) and Bombicci (1878), and which is also reported on the label of the dinite specimen stored in the Mineralogical Museum. Moreover, this same locality is also reported by Dufrenoy (1859), but the name is incorrectly written as "Zastagnana"; this may be the result of a misreading of first-hand information, probably a hand-written let-

ter by Meneghini himself. An incorrect locality (Lunigiana) was indicated by Petri (1852). Petri was a chemist, and it is possible that he was not very concerned with giving the exact description of the locality at which the dinite was found. This incorrect locality was reported by Dana (1854), and after Dana by most authors – but not Italian ones – who have included dinite in different mineralogical treatises (*e.g.* Doelter & Leitmeier, 1931; Hintze, 1933).

As a matter of fact there is no doubt that our sample corresponds to the mineral examined by the older authors; the general appearance of our material is consistent with the first description of dinite. The chemical formula reported on the label –  $C_{18}H_{16}$  – is just the one suggested by Petri (1852). In this regard, it should be stressed that the analytical data obtained by Petri (1852) are correct. The erroneous formula derives merely from an incorrect assignment of the atomic weights (2 instead of 1 for hydrogen, in this case) during the middle of the last century.

### New data for dinite

#### 1) Chemical analysis

The only previous available chemical analysis of dinite is reported in Petri (1852). We carried out a further chemical analysis on the same material using a Carlo Erba 1104 elemental micro-analyser. The data are compared in Table 1. Both analyses indicate  $C_{20}H_{36}$  as the most probable formula for dinite.

#### 2) Density

The measured density of dinite, obtained by microfloatation, is  $1.01 \pm 0.01$  g/cm<sup>3</sup>, which closely matches the calculated value of 1.02 g/cm<sup>3</sup>.

Table 1. Chemical analyses of dinite.

wt. %	Petri (1852)	This work	"Ideal"
C	87.11	86.77	86.88
H	12.89	13.44	13.12
Total	100.00	100.21	100.00
Chemical formula (on the basis of 20 carbon atoms)			
	$C_{20}H_{35.26}$	$C_{20}H_{36.91}$	$C_{20}H_{36}$

### 3) Fusion point

The fusion point of our material was measured at 33-34°C using Kopffler apparatus, in close agreement with the value (<35°C) given by Ciusa & Galizzi (1921).

### 4) Solubility

Dinite is very soluble in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CCl}_4$  and  $\text{C}_6\text{H}_5(\text{CH}_3)$  and poorly soluble (only when heated) in  $\text{CH}_3\text{OH}$  and  $\text{C}_2\text{H}_5\text{OH}$ .

### 5) Molecular weight

This was determined with a VG70 mass spectrometer, working at 70 eV, by direct introduction of the sample. The sample consisted of a few representation crystals obtained by slow evaporation of a solution of dinite in absolute ethanol. The obtained molecular weight of dinite is 276. The mass spectrum (Fig. 1) indicates the loss of a  $\text{CH}_3$  and a  $\text{CH}_2\text{-CH}_3$  fragment.

### 6) Nuclear Magnetic Resonance

The  $^1\text{H-NMR}$  spectrum, obtained with a Varian Gemini 200 spectrometer, is reported in Fig. 2. The singlets around 0.80 ppm indicate the occurrence of methyl groups ( $-\text{CH}_3$ ),

which are linked to tertiary C atoms. The absence of signals in the range 2-8 ppm indicates a lack of aromatic protons as well as double or triple bonds.

### 7) Infrared spectrum

The IR spectrum was obtained with a Perkin-Elmer FTIR 1600 spectrometer using a solution of dinite in "Nujol", (see Fig. 3). The spectrum presents the typical features of a saturated hydrocarbon.

### 8) X-ray diffraction

Single crystal Weissenberg photographs showed dinite to be orthorhombic with space group  $P2_12_12_1$ . The powder diffraction pattern of dinite was obtained with a Gandolfi camera and the results reported in Table 2. The indexing of the Gandolfi pattern was carried out with the help of the collected intensity data. The refinement of the cell constants was performed on a four-circle diffractometer (see below).

## Structural analysis

A single crystal structural study was carried out on a crystal obtained by slow evaporation of a solution of dinite in ethanol. The recrystal-

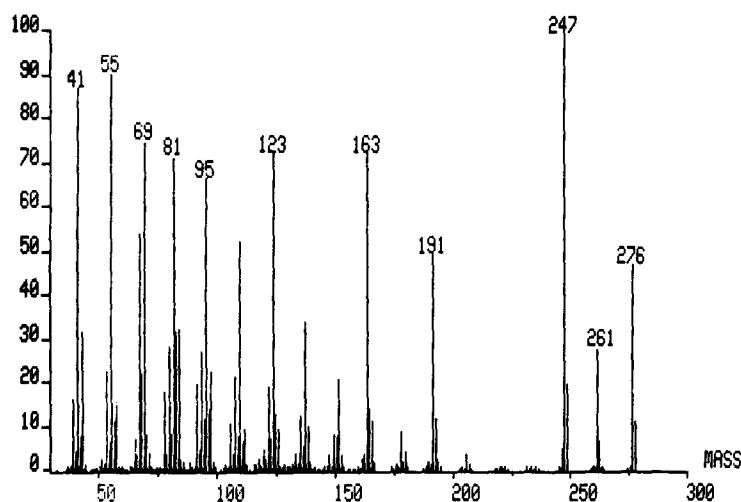


Fig. 1. Mass spectrum of dinite. The intensity of the peaks is given in % with respect to the strongest peak.

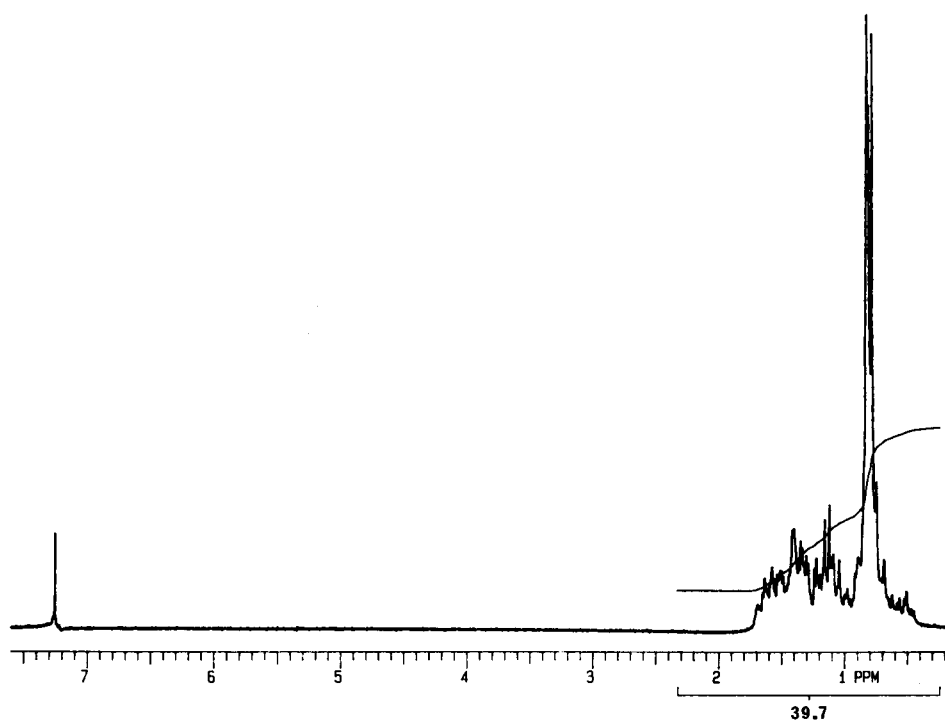


Fig. 2. <sup>1</sup>H-NMR spectrum of dinitite (200 MHz, CDCl<sub>3</sub>). The line at 7.3 ppm is due to the solvent.

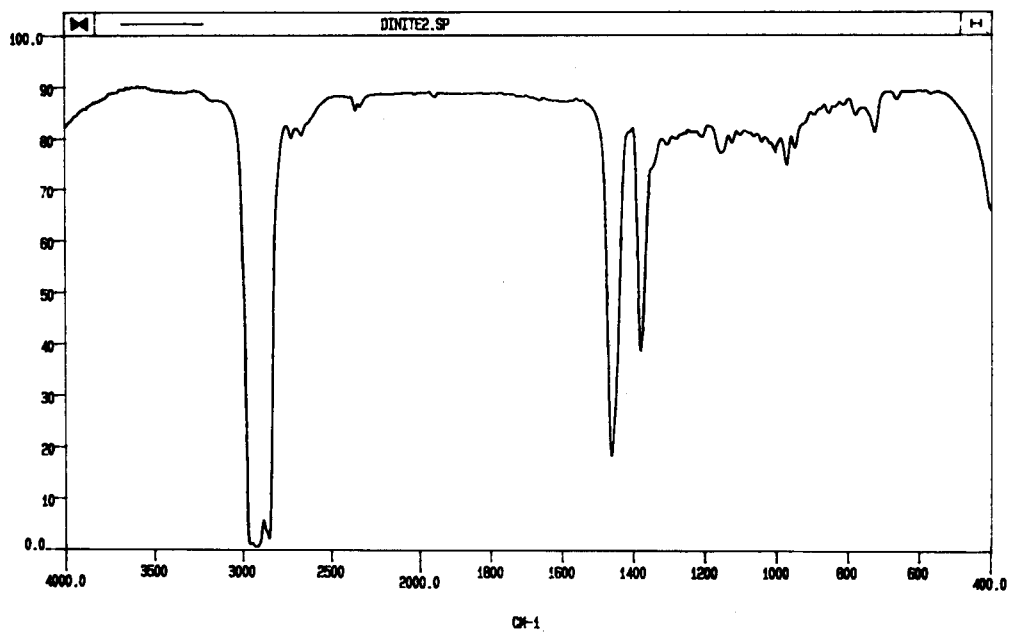


Fig. 3. IR spectrum of dinitite.

Table 2. Powder pattern of dinite (Gandolfi camera,  $\text{CuK}\alpha$ ,  $\lambda = 1.54178 \text{ \AA}$ ).

I	$d_{\text{obs}}$	$d_{\text{calc}}$	hkl	I	$d_{\text{obs}}$	$d_{\text{calc}}$	hkl
ms	8.92	8.88	110	m	2.982	2.982	141
ms	8.32	8.39	101	w	2.900	2.904	411
s	7.00	7.01	111	w	2.835	2.835	240
mw	6.36	6.38	020	mw	2.745	2.751	241
w	6.14	6.18	200	m	2.696	2.702	421
vw	5.76	5.71	002	w	2.494	2.491	051
vs	5.53	5.57	021	m	2.432	2.426	510
vs	5.06	5.08	121	m	2.301	2.304	520
mw	4.80	4.80	112	mw	2.251	2.259	521
w	4.44	4.44	220	m	2.173	2.179	441
vw	4.16	4.19	202	m	2.173	2.170	350
		4.14	221	mw	2.143	2.137	530
		4.02	122	m	2.094	2.100	531
ms	4.02	4.02	130	w	2.025	2.028	352
m	3.870	3.875	301	mw	1.994	1.993	062
m	3.793	3.794	131	mw	1.966	1.968	450
mw	3.706	3.708	311	mw	1.923	1.926	541
mw	3.502	3.505	222	w	1.849	1.849	542
w	3.412	3.412	032			1.749	272
		3.312	321	mw	1.748	1.748	710
mw	3.303	3.289	132	w	1.667	1.667	370
mw	3.235	3.232	312	w	1.644	1.650	371
mw	3.066	3.073	041				

lized material turned out to be identical to the natural one, since the Gandolfi patterns were the same. The dimensions of the crystal were *ca.* 0.8 x 0.7 x 0.4 mm. Dinite is orthorhombic, space group  $P2_12_12_1$ , with  $a = 12.356(4)$ ,  $b = 12.762(4)$ ,  $c = 11.427(3) \text{ \AA}$ . The intensity data were measured on an Italcristal Structures four-circle automatic diffractometer, using graphite-monochromatized  $\text{MoK}\alpha$  radiation. 1420 reflections were measured in  $\Theta$ - $2\Theta$  scan mode, scan range in  $\Theta$  ( $1.2 + 0.3 \tan \Theta$ ) $^\circ$ , scan speed  $2^\circ \text{ min}^{-1}$ ,  $2\Theta_{\text{max}} 46^\circ$ . Of the measured intensities, those having  $I > 2.5 \sigma(I)$  were considered as observed and were then used in the least-square calculations after reduction for Lorentz and polarization factors. Absorption corrections were performed by DIFABS (Walker & Stuart, 1983). The structure was solved with direct methods using SHELXS86 (Sheldrick, 1986) and refined using SHELX76 (Sheldrick, 1976) packages. The positions of the hydrogen atoms were computed using AFIX cards of the SHELX76 program. All hydrogens were assigned the same  $U$  isotropic temperature factor, which has been refined to 0.120(7). Final reliability indices are:  $R = 0.068$ ,  $R_w = 0.075$  ( $w = 1/[\sigma^2(F_o) + 0.0048(F_o)^2]$ ), for 787 unique reflections. The asymmetric unit of dinite is represented in Fig. 4; the final positional and thermal parameters are reported in Table 3, whereas bond lengths are reported in

Table 4. The C-C bonds range from 1.512 to 1.608  $\text{Å}$ , which confirms the absence of double C=C bonds and aromatic cycles, as well as the correctness of  $\text{C}_{20}\text{H}_{36}$  as the structural formula for dinite. As the shortest intermolecular C...C contact is 3.84(1)  $\text{Å}$ , the molecular packing results only from van der Waals interactions.

## Conclusions

The present data indicate that the organic mineral dinite is an alicyclic saturated hydrocarbon with three condensed cycles, as shown in Fig. 4. The correct formula for the mineral is  $\text{C}_{20}\text{H}_{36}$ , and its chemical name is 1-ethyl-1,5,5',13-tetramethyl-perhydrophenanthrene.

Similar hydrocarbon minerals, derivatives of phenanthrene, are described as fichtelite,  $\text{C}_{19}\text{H}_{34}$  (Strunz, 1962), or hartite (bombiccite),  $\text{C}_{20}\text{H}_{34}$  (Foresti Serantoni *et al.*, 1978) and are found in lignite deposits. This suggests a possible relation of such minerals with the abietic acid, the most abundant component of the resinic acids.

In the light of the new data obtained on the same specimen of dinite originally described by Petri (1852), we propose a re-definition of dinite from Castelnuovo Garfagnana as a distinct mineralogical species. Obviously, the old name dinite should be maintained. The type specimen is preserved in the "Museo di Storia

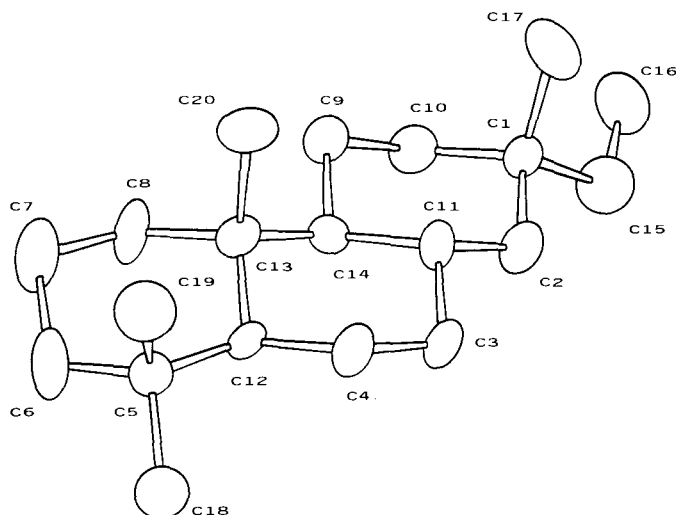


Fig. 4. ORTEP/II (Johnson, 1976) sketch of the asymmetric unit of dinite with labelling of atoms.

Table 3. Fractional coordinates and equivalent U isotropic ( $\text{\AA}^2$ ) thermal parameters for dinite.

Atom	x	y	z	U
C1	0.0801(6)	0.6792(6)	0.2410(7)	0.050(3)
C2	0.1657(7)	0.6988(8)	0.3341(8)	0.064(4)
C3	0.3429(7)	0.6572(7)	0.4333(7)	0.059(3)
C4	0.4456(6)	0.5917(7)	0.4316(7)	0.057(3)
C5	0.6155(6)	0.5462(8)	0.3087(8)	0.057(3)
C6	0.6582(7)	0.5509(11)	0.1834(9)	0.093(5)
C7	0.5835(8)	0.4998(10)	0.0932(10)	0.106(5)
C8	0.4703(7)	0.5498(10)	0.0960(8)	0.088(5)
C9	0.2321(6)	0.5929(8)	0.1233(8)	0.068(4)
C10	0.1384(7)	0.6733(7)	0.1233(8)	0.062(4)
C11	0.2622(6)	0.6238(7)	0.3397(7)	0.050(3)
C12	0.4970(6)	0.5886(7)	0.3103(7)	0.050(3)
C13	0.4176(7)	0.5467(7)	0.2179(8)	0.057(3)
C14	0.3157(6)	0.6177(6)	0.2192(7)	0.048(3)
C15	-0.0000(8)	0.7724(8)	0.2448(11)	0.088(4)
C16	-0.0946(8)	0.7672(9)	0.1610(10)	0.092(5)
C17	0.0188(7)	0.5760(9)	0.2661(10)	0.082(4)
C18	0.6874(8)	0.6174(8)	0.3831(10)	0.080(4)
C19	0.6271(8)	0.4359(9)	0.3640(11)	0.095(5)
C20	0.3800(8)	0.4282(8)	0.2431(11)	0.093(4)

Table 4. Bond distances ( $\text{\AA}$ ) in dinite.

C1 - C2	1.521(12)	C5 - C19	1.550(15)
C1 - C10	1.528(12)	C6 - C7	1.530(15)
C1 - C15	1.548(13)	C7 - C8	1.538(14)
C1 - C17	1.546(13)	C8 - C13	1.538(13)
C2 - C11	1.530(12)	C9 - C10	1.547(12)
C3 - C4	1.520(12)	C9 - C14	1.539(11)
C3 - C11	1.523(11)	C11 - C14	1.529(11)
C4 - C12	1.525(11)	C12 - C13	1.537(12)
C5 - C6	1.527(13)	C13 - C14	1.551(11)
C5 - C12	1.561(11)	C13 - C20	1.608(14)
C5 - C18	1.529(14)	C15 - C16	1.512(15)

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### References

- Bombicci, L. (1878) : Corso di mineralogia. Vol. II. 2nd ed. Bologna, Zanichelli, 528 pp.
- Ciusa, R. & Galizzi, A. (1921) : Ricerche su alcuni costituenti delle ligniti. *Gazz. Chim. It.*, **51**, 55-60.
- Cocchi, I. (1856) : Description des roches ignées et sédimentaires de la Toscane dans leur succession géologique. *Bull. Soc. Géol. France, ser. II*, **13**, 226-292.
- D'Achiardi, A. (1873) : Mineralogia della Toscana. Vol. II. Pisa, Tipografia Nistri, 402 pp.
- Dana, J.D. (1854) : A system of mineralogy. Vol. II. 4th ed. New York, George P. Putnam & Co., 533 pp.
- Doelter, C. & Leitmeier, H. (1931) : Handbüch der Mineralchemie. Band IV-3. Dresden, Verlag von Theodor Steinkopff, 1174 pp.
- Dufrenoy, A. (1859) : Traité de minéralogie. Vol. IV. 2nd ed. Paris, Dalmont et Dunod, 770 pp.
- Foresti Serantoni, E., Krajewski, A., Mongiorgi, R., Riva di Sanseverino, L. & Sheldrick, G.M. (1978) : The crystal and molecular structure of a mineral diterpene, bombicite, C<sub>20</sub>H<sub>34</sub>. *Acta Cryst.*, **B34**, 1311-1316.
- Hintze, C. (1933) : Handbüch der Mineralogie. Band I-4. Berlin, Walter De Gruyter & Co., 1454 pp.
- Johnson, C.K. (1976) : ORTEP II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, U.S.A.
- Petri, G. (1852) : Sulla dinite, nuovo minerale di origine organica. *Gazz. Med. Ital., Toscana, ser. II*, **4**, 233-234.
- Sheldrick, G.M. (1976) : SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.
- (1986) : SHELXS86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
- Strunz, H. (1962) : Fichtelit, Dimethyl-isopropyl-perhydro-phenanthren. *Naturwiss.*, **49**, 9-10.
- (1978) : Mineralogische tabellen. Leipzig, Akademische Verlagsgesellschaft, 621 pp.
- Walker, N. & Stuart, D. (1983) : An empirical method for correcting diffractometer data for absorption effects. *Acta Cryst.*, **A39**, 158-166.

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