RAMAN SPECTRA OF ACENAPHTHENE AND ACENAPHTHENE-D_{10}

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ABSTRACT

The Raman spectra of acenaphthene and acenaphthene-d_{10} have been recorded with the help of a Spex Recording Raman Spectrophotometer using He-Ne Laser source (exciting line 6328 A of Neon). Detailed vibrational assignments of all the sixty fundamental frequencies have been made.

INTRODUCTION

THE vibrational spectrum of acenaphthene has been investigated by several workers in the infrared[1] and in Raman spectra.[2-4] The infrared spectra in polarized light of acenaphthene crystals and molecular vibrations have been investigated by Colombo[5] who assigned 47 fundamental frequencies. The present work deals with the Raman spectra of acenaphthene and its isotopic derivative. Detailed assignments of all the vibrational frequencies have been proposed. The study of the isotopic molecule together with polarization measurement has helped considerably in the vibrational assignment.

EXPERIMENTAL

The chemical acenaphthene was of E-Merck grade. Acenaphthene-d_{10} was obtained from CEA, Department des Radioelements, France. Raman spectra have been recorded with the help of a Spex Recording Raman Spectrophotometer using He-Ne Laser source. The exciting line is 6328 Å of Neon. Spectra have been recorded for two different orientations, normal to each other, of the sample. Figure 1 (a) and (b) show the Raman spectra of the two molecules.

RESULTS AND DISCUSSION

The crystal spectra of the molecule acenaphthene was investigated by Banerjee[6] and Kitaigorodskii.[7] A refined analysis of the molecule was given by Ehrlich.[8] From these works it has been concluded that the molecule of acenapthene ($C_{12}H_{10}$) belongs to the point group C_{2v}. All the carbon atoms and hydrogen atoms bonded to the aromatic rings lie in the plane of the molecule whereas each of the two CH_2 groups forms a plane normal to the molecular plane.

The sixty fundamentals of acenaphthene molecule are distributed among the four sym-

metry species $20 A_1 + 10 A_2 + 11 B_1 + 19 B_2$. The selection rules and vibrational analysis of an isolated molecule are given[5,9] in Table I. The vibrational analysis has been made using the empirical position and intensity rules. The magnitude of the isotopic shift R, the ratio of the frequency of a vibration in the normal molecule to the corresponding frequency in the deuterated molecule has been utilised to measure the correctness of the choice of frequencies in a given species. The values of R associated with different modes of vibrations in benzene and naphthalene are given in Table II. These values have been used as standard ones to identify similar vibrations in acenaphthene and acenaphthene-d_{10}. In interpreting the Raman spectra aid has been taken from the vibrational assignment of the naphthalene molecule.[10-14]

TABLE I

Selection rules and vibrational assignment for acenaphthene

	Selection rules			No. of vibrations	
Type	Raman	i.r.	C–C		C–H
A_1	P.	$\epsilon_{jk}=0$	M	$6t+5a$	$3s+3\beta+1S+1d+1\triangle$
A_2	D.	$\epsilon_{uw}\neq0$	I	4δ	$3\gamma+1S+1d+1\triangle$
B_1	D.	$\epsilon_{uv}\neq0$	M	5δ	$3\gamma+1S+1d+1\triangle$
B_2	D	$\epsilon_{vw}\neq0$	M	$5t+5a$	$3s+3\beta+1S+1d+1\triangle$

s=stretching, a=skeletal in-plane deformation, t=C–C stretching, β=in-plane bending δ=skeletal out of-plane bending, S=C–H stretching in CH_2 group, d=C–H bending in CH_2 group, $\triangle$=twisting and rocking of CH_2 group.

TABLE II

Spectral regions, mode of vibrations and values of R in benzene and naphthalene

Region	Mode of vibration	R
2900–3100	C–H stretching	1.30–1.35
1300–1670	C–C stretching	1.05
900–1050	Ring breathing	..
1000–1500	C–H in-plane bending	1.20–1.28
700–1200	C–H out-of-plane bending	1.20 1.28
1000	Skeletal deformation i.p.	1.05
700	Skeletal deformation o.p.	1.10

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VIBRATIONAL ASSIGNMENT

Ten C–H stretching vibrations are expected with distribution as $4A_1 + 1A_2 + 1B_1 + 4B_2$. We have assigned them as

A_1 (3050, 3030, 2923, 2856)
A_2 (2931)
B_1 (2984)
B_2 (3111, 3079, 2960, 2907)

$C_{12}H_{10}$ and $C_{12}D_{10}$. The values of R have been included in the last column of the table. It may be seen that the values of R observed for the C–H stretching modes of vibrations lie in the region 1·29–1·36, which is in agreement with similar observations in naphthalene. The vibrations characteristic of the CH_2 groups are assigned with the help of the assignments made by Herzberg[15] for C_2H_4O. In C_2H_4O (ethylene
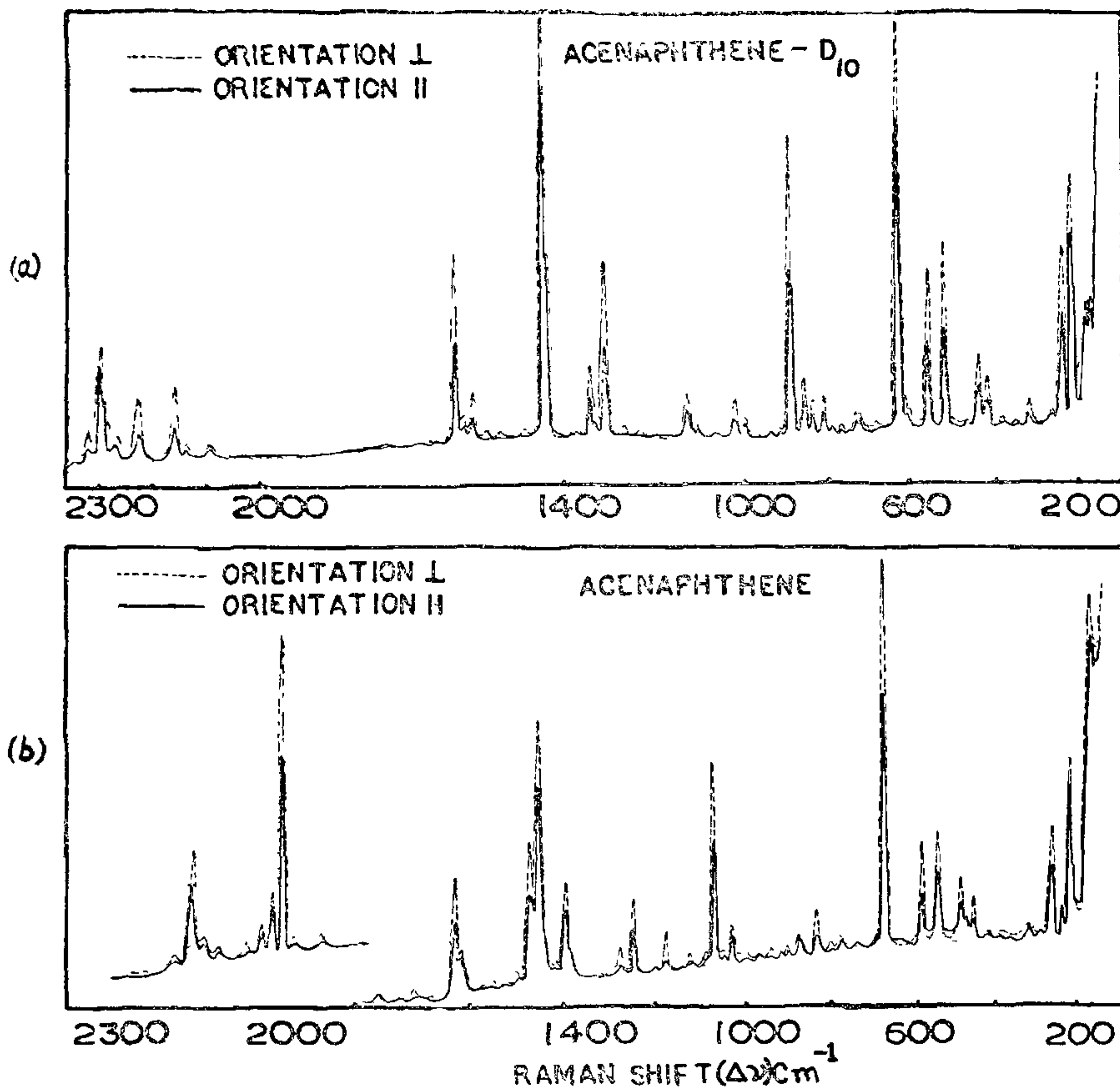

FIG. 1 (*a-b*)

The assignment of these modes of vibrations can be compared to the infrared spectrum of the crystal.[5] It is easy to assign the corresponding C–D stretching frequencies in the deuterated molecule from observation of intensities and shape of the bands. Table III gives the detailed vibrational assignment of

oxide) the CH_2 groups lie in a plane normal to the C–O–C ring.

A_1 Species

$(6t + 5a + 3s + 3\beta + 1S + 1d + 1\Delta)$

Four C–H stretching modes are observed as 3054, 3030, 2923 and 2856 cm^{-1}. The band at

Table III

Vibrational assignment of acenaphthene and acenaphthene-d_{10}

S.N.	Species	Type	$C_{12}H_{10}$	$C_{12}D_{10}$	R
1	A_1	ν (C–H)	3054	2294	1·33
2		ν (C–H)	3030	2270	1·29
3		ν (C–H)	2923	2159	1·35
4		ν (C–H)	2856	2103	1·36
5		ν (C–C)	1627	1617	1·01
6		ν (C–C)	1617	1597	1·01
7		ν (C–C)	1502	1410	1·06
8		ν (C–C)	1424	1372	1·04
9		ν (C–C)	1393	1309	1·06
10		CH_2 rocking	1278	1107	1·15
11		β (C–H)	1440	1200	1·20
12		β (C–H)	1245	1024	1·22
13		β (C–H)	1176	976	1·20
14		β (C–H)	1122	939	1·19
15		α (C–C–C)	939	902	1·05
16		α (C–C–C)	673	628	1·07
17		α (C–C–C)	572	558	1·02
18		α (C–C–C)	476	437	1·09
19		α (C–C–C)	465	442	1·05
20		ν (C–C)	1054	882	1·19
21	A_2	ν (C–H)	3079	2301(depol)	1·34
22		β (C–H)	1340	1290	1·04
23		CH_2 twisting	1023	..	..
24		γ (C–H)	1042	..	..
25		γ (C–H)	915	..	..
26		γ (C–H)	870	..	..
27		δ (C–C–C)	382	..	..
28		δ (C–C–C)	289	260	1·11
29		δ (C–C–C)	202	..	..
30		δ (C–C–C)	166	153(depol)	1·08
31	B_1	ν (C–H)	2984	2242	1·33
32		γ (C–H)	1440	1152	1·25
33		CH_2 rocking	1382	1270	1·08
34		γ (C–H)	965	764	1·26
35		γ (C–H)	832	731	1·14
36		γ (C–H)	798	724	1·10
37		δ (C–C–C)	776	616	1·25
38		δ (C–C–C)	448	417	1·07
39		δ (C–C–C)	269	250	1·08
40		δ (C–C–C)	233	214	1·09
41		δ (C–C–C)	214	177	1·21
42	B_2	ν (C–H)	3111	2317	1·34
43		ν (C–H)	2931	2187	1·34
44		ν (C–H)	2960	2227	1·33
45		ν (C–H)	2907	2140	1·36
46		ν (C–C)	1780	..	..
47		ν (C–C)	1765	..	..
48		ν (C–C)	1595	..	..
49		ν (C–C)	1496	1390	1·07
50		ν (C–C)	1475	1437	1·03
51		β (C–H)	1455	1340	1·08
52		β (C–H)	1199	998	1·20
53		CH_2 rocking	1150	..	..
54		β (C–H)	1085	917	1·18
55		β (C–H)	899	787	1·14
56		α (C–C–C)	535	518	1·04
57		α (C–C–C)	493	465	1·06
58		α (C–C–C)	413	..	..
59		α (C–C–C)	318	315	1·01
60		α (C–C–C)	262	236	1·11

3054 cm^{-1} corresponds to the frequency 3050 cm^{-1} in the infrared spectrum of the crystal.[5] This was identified as the C–H stretching band in CH_2 group due to an intense Davidov splitting.[5] The frequencies 1278 and 1440 cm^{-1} have been identified as the CH_2 rocking and CH_2 bending corresponding to the frequencies of 1310 and 1416 cm^{-1} in the crystal spectrum.[5] The ring breathing mode of vibration has been assigned to the very strong band at 1054 cm^{-1}. Its isotopic counterpart has been identified as the very strong band at 882 cm^{-1}. The observed ratio of R $=.1·19$ is equal to that observed for naphthalene.[14] The ring breathing mode shows a higher value as compared to the corresponding value in the crystal spectrum (1044 cm^{-1}). Other frequencies have been assigned with the help of the data of the crystal spectrum and the isotopic shifts expected.

A_2 Species

$$(4 \delta + 3 \gamma + 1 S + 1 \ d + 1 \triangle)$$

All the ten vibrations of this class are recorded. In the crystal spectrum, only three frequencies were identified. There was a frequency at 1938 cm^{-1} which was attributed as the A_2 type vibration by Colombo.[5] The present Raman spectrum does not show any band with this frequency. The frequency 1340 cm^{-1} has been assigned as the C–H bending mode in CH_2 group corresponding to the frequency 1352 cm^{-1} in the crystal spectrum. In the Raman spectrum of ethylene oxide[15] the CH_2 rocking mode has been assigned to the frequency 1379 cm^{-1}. The C–H stretching frequency in CH_2 group has been identified by Herzberg at 3061 cm^{-1} which is depolarized. In acenaphthene and acenaphthene-d_{10}, the frequencies 3079 and 2301 cm^{-1} are assigned as C–H and C–D stretching modes. These frequencies are also depolarized.

B_1 Species

$$(5 \delta + 3 \gamma + 1 S + 1 d + 1 \triangle)$$

Eleven B_1 modes of vibrations could be easily identified. The frequency 2984 cm^{-1} has been assigned as the C–H stretching mode in CH_2 group corresponding to the value 3007 cm^{-1} (polarized) assigned by Herzberg. Other out-of-plane modes are assigned with the help of the comparison made with naphthalene spectrum.

B_2 Species

$$(5 t + 5^a + 3 s + 3 \beta + 1 S + 1 d + 1 \triangle)$$

The frequencies of this class have also been assigned with the help of a comparison with the crystal spectrum and the naphthalene

spectrum. However, all the isotopic counter-parts could not be identified.

As regards the degree of depolarization, it has been observed that for totally symmetric vibrations, the values lie between 0 and 6/7. For many vibrations, however, the degree of depolarization could not be precisely determined.

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1. Richards, R. E. and Thompson, H. W., *Proc. Roy. Soc.* (London), 1941, **195 A**, 1.
2. Manzoni. R., *Atti. Acad. Nazl. Lincei, Rend. Classe. Sci. Fis. Mat. Nat,* 1935, **21**, 166.
3. Luther, H. and Reichel, C., *Z. Physik. Chem.*, 1950, **195**, 103.
4. Mathieu, J. P., Ecollan, M. and Ecollan, J. F., *J. Chem. Phys.*, 1954, **50**, 250.
5. Colombo, L., *Ibid.*, 1963, **39**, 1942
6. Banerjee, K, and Sinha, K., *Indian J. Phys.*, 1937, **21**, 21.
7. Kitaigorodskii, A. I., *Zh. Fiz. Khim.*, 1949, **23**, 1036.
8. Ehrlich, H. W., *Acta Cryst.*, 1957, **10**, 699.
9. Wilson, B. Jr., Decius, J. C. and Cross, P. C., *Molecular Vibrations*, McGraw-Hill Book Company, Inc., New York, 1956.
10. Lippincott, E, R. and O'Reilly, E. J., *J. Chem. Phys.*, 1955, **23**, 238.
11. Person. W. B , Pimental, G. C. and Schnepp, O., *Ibid.*, 1955, **23**, 230.
12. Scully, D. B. and Whiffen, D. H., *Spectrochim. Acta*, 1960, **16**, 1409.
13. — and —, *J. Mol. Spectry.*, 1957, **1**, 257.
14. Bree, A. and Kydd, R. A., *Spectrochim. Acta*, 1970, **26 A**, 1791.
15. Herzberg, G., *Molecular Spectra and Molecular Structure*, D. Van Nostrand, Inc., Princeton, New Jersey, 1959, p. 341.

A NOTE ON THE OCCURRENCE OF BENSTONITE, A CARBONATE OF CALCIUM AND BARIUM FROM THE CARBONATITE COMPLEX AT JOGIPATTI, NEAR SAMALPATTI, DHARMAPURI DISTRICT, TAMIL NADU

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ABSTRACT

Benstonite, a carbonate of calcium and barium has so far been reported from two other localities in the world, *viz.*, from Argansas, U.S.A. (Lippman, 1962) and Längbam, Sweden (Sandius, 1963). This paper deals briefly with the mineralogy and petrogenesis of a new occurrence from Jogipatti, India. Benstonite at Jogipatti is related to the carbonatites in which it occurs in a massive form. From the field data it is concluded that the formation of benstonite took place at high temperature, although it is generally postulated that the introduction of barium is an indication of late low temperature activity. However in the area under consideration, benstonite is associated with coarse black pyroxene and white feldspar which are usually high temperature minerals.

IN 1968, during the course of a detailed field examination of the carbonatite occurrences near Koratti, the authors recognised several other satellite bodies of carbonatites out of which the occurrence near Jogipatti drew special attention in that they came across a massive light yellow carbonate which looked rather different from the other carbonate minerals usually associated with carbonatites. This mineral has subsequently been identified as benstonite.

Jogipatti is a small village situated about 1·5 kilometres north of Samalpatti R.S. lying on the Tirupathur-Salem Broad Gauge Sec-tion of the Southern Railway. It falls in Uttangarai Taluk of Dharmapuri District in the State of Tamil Nadu (*Survey of India Toposheet* 57 L/7).

The principal rocks encountered in the area are syenites in which occur carbonatites, pyroxene pegmatites and veins of quartz barytes. The syenites are mostly made up of alkali feldspar with a few ferromagnesium and other accessory minerals. The carbonatites occur as small lenses within the syenites. About seven such bodies were noticed in the field. The dimension of the individual bodies varies widely. They are generally elongated in