

VIBRATIONAL SPECTROSCOPIC STUDIES AND AB INITIO CALCULATIONS OF 4-tert butyl BENZYL SELENOCYANATE

L.Usha Kumari^a, M.Fathima Beegum^a, B.Harikumar^b, Hema Tresa Varghese^c, C.Yohannan Panicker^{a*}

^aDepartment of Physics, TKM College of Arts and Science, Kollam, Kerala, India.

^bDepartment of Chemistry, TKM College of Arts and Science, Kollam, Kerala, India.

^cDepartment of Physics, Fatima Mata National College, Kollam, Kerala, India.

*E-mail: cyphyp@rediffmail.com

ABSTRACT

FT-IR spectrum of 4-tert butyl benzyl selenocyanate is recorded and analysed. The vibrational wavenumbers have been calculated using the Hartree-Fock method. Comparison of the observed fundamental vibrational wavenumbers of 4-tert butyl benzyl selenocyanate with calculated results by Hartree-Fock method is found in agreement with the experimental data. Predicted infrared and Raman intensities are reported.

Keywords : FT-IR, Selenocyanate, HF ab initio calculations.

INTRODUCTION

Organoselenium compounds have shown promising results in a variety of chemopreventative studies by Reddy *et al.*¹ focusing on mammary and colon tumours in rats, in which tumour formation was induced with 7, 12-dimethylbenz(a)anthracene (mammary tumours) or azoxymethane (colon tumours)^{2,3}. Inhibition of tumour formation by dietary organoselenium supplementation was compared to controls and animals fed inorganic selenium supplements. The p-methoxy-benzyl selenocyanate and p-phenylenebis(methylene)selenocyanate are most effective at preventing azoxymethane induced colonic aberrant foci and p-phenylenebis(methylene)selenocyanate best suppressed induced mammary tumours⁴. Ganther⁵ reviewed some of the potential mechanisms for chemoprevention due to selenium's effects on the activity of cellular proteins. Possibilities include the effect selenium compounds have on increasing apoptosis, supplementing the activity of selenoproteins such as glutathione peroxidase or thioredoxin reductase, and inhibition of enzymes including protein kinase C and thymidine kinase⁶. Although, selenium is an essential trace nutrient⁷, it is a poison at concentrations exceeding about 4 mg/kg. Benzyl selenocyanate, a synthetic organoselenium compound, has been shown to inhibit chemically induced tumours in several animal model systems⁸. Ab initio quantum mechanical method is at present widely used for simulating IR spectra. Such simulations are indispensable tools to perform normal coordinate analysis so that modern vibrational spectroscopy is unimaginable without involving them. In the present study the FT-IR and theoretical calculations of the wavenumbers of the title compound are reported.

EXPERIMENTAL

The FT-IR spectrum was recorded using a Perkin-Elmer FT-IR 1760X spectrometer. The spectral resolution was 4 cm⁻¹. Standard KBr technique with 1 mg sample per 300 mg KBr was used. Benzyl selenocyanates can be made from the corresponding benzylic halides in 30-60 minutes using acetonitrile as a solvent. A solution of KSeCN (2.2 mmol) in acetonitrile (5 mL)

was added to a stirred solution of the benzylic halide (2 mmol) in acetonitrile (15 mL). The flask containing KSeCN was rinsed with additional solvent (1 – 2 mL) after the end of the addition and this was also added to the reaction. The formation of a fine white precipitate (KBr-KCl) signaled the progress of the reaction. Reactions were deemed complete when no additional precipitate formed (30 -60 min.). This was verified by thin layer chromatography. The reaction was poured into distilled water (200 mL) and stirred for about 30 minutes. After this time, the mixture was cooled in ice and vacuum filtered. The solid precipitate was washed generously with water to remove any excess salts. The crude solid was then purified using a mixed crystallization from benzene/toluene (1:1) to dissolve the solid and heptane to induce the cloud point. The general synthetic procedure and elemental analyses were reported by Jacob *et al.*⁴.

COMPUTATIONAL DETAILS

Calculations of the title compound were carried out with Gaussian03 program⁹ using the HF/6-31G* basis set to predict the molecular structure and vibrational wavenumbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using the analytic second derivatives to confirm the convergence to minima of the potential surface. The wavenumber values computed at the Hartree-Fock level contain known systematic errors due to the negligence of electron correlation¹⁰. We therefore, have used the scaling factor value of 0.8929 for HF/6-31G* basis set. The absence of imaginary wave numbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The assignments of the calculated wave numbers are aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes^{11,12}.

RESULTS AND DISCUSSION

The observed IR bands with the relative intensities and calculated wave numbers and assignments are given in Table 1. Nitrogen Compounds featuring triple or cumulated double bonds such as cyanides or nitriles ($-C\equiv N$), all provide a unique spectrum, typically with a single, normally intense absorption at $2280-2200\text{ cm}^{-1}$ (for cyano compounds) and $2285-1990\text{ cm}^{-1}$ (for cyanates, isocyanates and thiocyanates)^{13,14}. Infrared wavenumbers of $C\equiv N$ stretching mode^{15,16}, in various thiocyanates and selenocyanate compounds are reported in the range $2157-2176\text{ cm}^{-1}$. In the present case the stretching mode $\nu_{C\equiv N}$ is observed at 2146 cm^{-1} in the IR spectrum. The calculated value for this mode is 2274 cm^{-1} .

The vibrations of the CH_2 group, the asymmetric stretch $\nu_{as}CH_2$, symmetric stretch ν_sCH_2 , scissoring vibration δCH_2 and wagging vibration ωCH_2 appear in the regions 2960 ± 20 , 2930 ± 10 , 1420 ± 20 and $1255 \pm 15\text{ cm}^{-1}$, respectively¹³. The HF calculations give $\nu_{as}CH_2$ at 2997 and ν_sCH_2 , 2936 cm^{-1} . The band observed at 2959 cm^{-1} in the IR spectrum is assigned as the symmetric ν_sCH_2 mode. The CH_2 deformation band¹⁷ which comes near 1463 cm^{-1} in alkenes is lowered to about 1440 cm^{-1} when the CH_2 group is next to a double or triple bond. The HF calculations give this mode at 1457 cm^{-1} and experimentally no band is observed. The CH_2 wagging mode is observed at 1226 cm^{-1} as a weak band in the IR spectrum and at 1227 cm^{-1} theoretically. The band calculated at 1176 cm^{-1} is assigned as the twisting mode τCH_2 . The rocking mode¹³ ρCH_2 is expected in the region $780 \pm 20\text{ cm}^{-1}$ and the wavenumber 782 cm^{-1} given by HF calculation is assigned as this mode.

For $-CH_2SCN$ ¹³, the antisymmetric CSC stretch which is associated with the S-CN stretching vibration, appears weakly to moderately at $685 \pm 15\text{ cm}^{-1}$, and the symmetric CSC

stretch, corresponding with the CH₂S stretching vibration, absorbs moderately to strongly in the range $635 \pm 26 \text{ cm}^{-1}$. The CH₂SCN group provides five skeletal deformations and a torsion, in which two R-C-S (R=C) skeletal deformations must be considered as external deformations¹³. For the title compound antisymmetric CSeC stretch, which is associated with the Se-CN stretching vibration appears strongly at 600 cm^{-1} and the symmetric CSeC stretch, corresponds with the CH₂-Se stretching vibration, absorbs moderately to strongly at 513 cm^{-1} in the IR spectrum. The ab initio calculations give these modes at 613 and 505 cm^{-1} respectively. The skeletal deformation bands $\delta\text{Se-CN}$ and $\gamma\text{Se-CN}$ are calculated to be in the low wavenumber region. The νCSe of SeC \equiv N is reported in the range $519 - 528 \text{ cm}^{-1}$ and the bending vibration of NCSe of SeC \equiv N at $418, 397$ and 365 cm^{-1} ¹⁷. For selenocyanate complexes the SeCN deformation bands¹⁸ are reported to be in the range $100-187 \text{ cm}^{-1}$. In the present case, the HF calculations give the deformation bands of SeCN at 423 and 422 cm^{-1} .

Although the tBu substituent can provide six methyl antisymmetric stretching vibrations¹³, generally only three are observed in the region $2900 - 2970 \text{ cm}^{-1}$. Experimentally no bands are observed and the HF calculations give the $\nu_{\text{as}}\text{Me}$ at $2914, 2914, 2922, 2925, 2927, 2930 \text{ cm}^{-1}$. Aromatic molecules give the methyl symmetric stretchings¹³ between 2915 and 2860 cm^{-1} . In the present case the weak bands observed at $2866, 2852 \text{ cm}^{-1}$ in the IR spectrum and calculated values at $2860, 2860, 2869 \text{ cm}^{-1}$ are assigned as the symmetric methyl stretching modes. The methyl antisymmetric deformations absorb between 1440 and 1490 cm^{-1} and the symmetric deformations in the range $1360 - 1400 \text{ cm}^{-1}$ ¹³. The bands observed at $1463, 1460, 1454 \text{ cm}^{-1}$ and $1411, 1360 \text{ cm}^{-1}$ are assigned as antisymmetric and symmetric deformations of the methyl group. The HF calculations give this modes at $1489, 1480, 1474, 1463, 1459, 1456 \text{ cm}^{-1}$ (antisymmetric) and $1409, 1389, 1387 \text{ cm}^{-1}$ (symmetric). Despite the fact that all three CC₃ stretching vibrations severely couple with the six methyl rocking modes, six absorption regions more or less overlapping one another can be assigned¹³. Most of the molecules display the methyl rocks in the region $890 - 1170 \text{ cm}^{-1}$, $\nu_{\text{as}}\text{CC}_3$ stretching in the region $1180 - 1275 \text{ cm}^{-1}$ and $\nu_{\text{s}}\text{CC}_3$ stretching in the range $790 \pm 55 \text{ cm}^{-1}$ ¹³. The antisymmetric, symmetric and rocking skeletal deformations of the CC₃ group are expected in the regions, $435 \pm 85, 335 \pm 80$ and $300 \pm 80 \text{ cm}^{-1}$ respectively¹³. The three methyl torsions¹³ are expected below 250 cm^{-1} . For the title compound, the bands at $1028, 1017, 942, 892 \text{ cm}^{-1}$ in the IR spectrum are assigned as ρMe bands. The ab initio calculations give the rocking modes at $1165, 1030, 1016, 939, 912$ and 904 cm^{-1} . The bands at 1267 (IR), $1264, 1224 \text{ cm}^{-1}$ (HF) are assigned as $\nu_{\text{as}}\text{CC}_3$ stretching modes. The HF calculations give $\nu_{\text{s}}\text{CC}_3$ stretching band at 821 cm^{-1} which is absent in the IR spectrum. The deformation bands of CC₃ are calculated to be at $445, 345, 329, 320$ and 286 cm^{-1} .

The CH stretching vibrations of the phenyl ring are observed at $3057, 3028, 3000 \text{ cm}^{-1}$ in the IR spectrum. The calculated values for these modes are $3046, 3024, 3001$ and 2998 cm^{-1} . According to Roeges¹³ νCH is expected in the region $3000 - 3100 \text{ cm}^{-1}$. The benzene ring possesses six ring stretching vibrations, of which the four with the highest wavenumbers (occurring respectively near $1600, 1580, 1490$ and 1440 cm^{-1}) are good group vibrations. With heavy substituents the bands tend to shift towards lower wavenumber side. In the absence of ring conjugation, the band at 1580 cm^{-1} , is usually weaker than that at 1600 cm^{-1} . In many cases, such as alkyl substitution, the 1580 cm^{-1} absorption is only a shoulder on the 1600 cm^{-1} band. In the case of C=O substitution the band near 1490 cm^{-1} can be very weak. The fifth ring stretching vibration is active near $1315 \pm 65 \text{ cm}^{-1}$. The sixth ring stretching vibration or ring breathing mode appears as a weak band near 1000 cm^{-1} in mono-, 1,3-di- and 1,3,5-tri-substituted benzenes. In the otherwise substituted benzenes, however, this vibration is substituent sensitive

and difficult to distinguish from the ring in-plane deformation. For the para di substituted light heavy benzene, the ν_{Ph} modes¹³ are expected in the range 1280 – 1620 cm^{-1} . For the title compound, the bands observed at 1638, 1511, 1330 cm^{-1} in the IR spectrum are assigned as the ring stretching modes. The calculated values for these modes are 1627, 1577, 1514, 1417 and 1317 cm^{-1} .

For para substituted benzenes, the δ_{CH} modes¹³ are seen in the range 995 – 1315 cm^{-1} and no bands are observed in the IR spectrum. The calculated values are 1205, 1084, 1063, 996 cm^{-1} .

The CH out-of-plane deformations¹³ are observed between 1000 and 700 cm^{-1} . Generally the CH out-of-plane deformations with the highest wavenumbers have a weaker intensity than those absorbing at lower wavenumbers. The very strong CH out-of-plane deformation band, occurring at $840 \pm 50 \text{ cm}^{-1}$ is typical for 1,4-disubstituted benzenes¹³. For the title compound, a very strong γ_{CH} is observed at 841 cm^{-1} in the IR spectrum. Again, according to the literature^{13,19} a lower γ_{CH} absorbs in the neighbourhood $820 \pm 45 \text{ cm}^{-1}$, but is much weaker or infrared inactive. The γ_{CH} modes are observed at 964, 841, 748 cm^{-1} in the IR spectrum. The ab initio calculations give these modes at 984, 970, 849, 742 cm^{-1} . The ring breathing mode²⁰ for the para substituted benzenes with entirely different substituents have been reported in the interval 780 – 840 cm^{-1} . The band at 829 cm^{-1} in the IR spectrum and 834 cm^{-1} (HF) is assigned as the ring breathing mode.

From the ab initio calculations, the carbon-carbon bond lengths in the phenyl ring lies between 1.3797 and 1.3974 Å and the C-H bond lengths in the range 1.0721 – 1.0742 Å. Here for the title compound, benzene is a regular hexagon with bond lengths somewhere in between the normal values of a single (1.54 Å) and a double (1.33 Å) bond²¹. The HF calculation also gives shortening of angle $\text{C}_5\text{-C}_6\text{-C}_1$ by 3° and increase of angle $\text{C}_1\text{-C}_6\text{-C}_{12}$ by 3.1° from 120° at C_6 position and this asymmetry of angles reveals the repulsion between methyl group and the phenyl ring²².

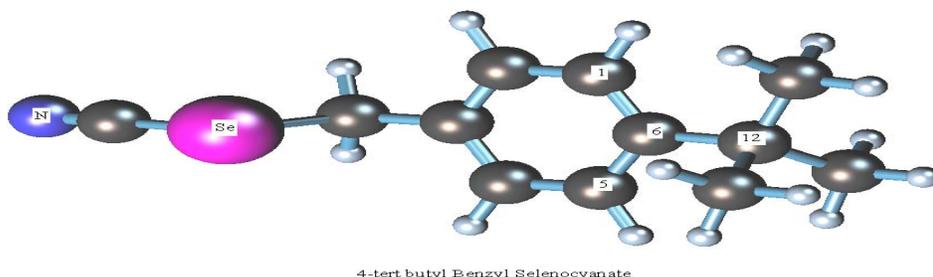
Table-1: Calculated vibrational wavenumbers, measured infrared band positions and assignments for 4-tert butyl benzyl selenocyanate

$\nu_{\text{(HF)}} (\text{cm}^{-1})$	$\nu_{\text{(IR)}} (\text{cm}^{-1})$	IR intensity (KM/Mole)	Raman activity ($\text{\AA}^4/\text{AMU}$)	Assignments
3046	3057 w	11.97	87.38	ν_{CH}
3024	3028 w	19.61	91.03	ν_{CH}
3001	3000 w	6.71	81.79	ν_{CH}
2998		16.16	47.55	ν_{CH}
2997		4.11	27.37	$\nu_{\text{as}}\text{CH}_2$
2936	2959 m	9.28	67.17	$\nu_{\text{s}}\text{CH}_2$
2930		66.98	77.23	$\nu_{\text{as}}\text{Me}$
2927		33.63	49.66	$\nu_{\text{as}}\text{Me}$
2925		120.09	230.76	$\nu_{\text{as}}\text{Me}$
2922		23.58	21.30	$\nu_{\text{as}}\text{Me}$
2914		6.60	21.61	$\nu_{\text{as}}\text{Me}$
2914		6.52	12.24	$\nu_{\text{as}}\text{Me}$
2869	2866 w	28.09	310.76	$\nu_{\text{s}}\text{Me}$
2860		32.60	2.32	$\nu_{\text{s}}\text{Me}$
2860	2852 w	29.16	5.48	$\nu_{\text{s}}\text{Me}$
2274	2146 s	20.87	180.97	$\nu_{\text{C}\equiv\text{N}}$
1627	1638 sbr	5.96	168.60	ν_{Ph}

1577		0.77	1.24	ν Ph
1514	1511 m	23.99	4.74	ν Ph
1489		4.93	2.87	δ_{as} Me
1480		5.09	19.26	δ_{as} Me
1474		6.17	19.92	δ_{as} Me
1463	1463 w	0.76	20.33	δ_{as} Me
1459	1460 m	0.05	12.47	δ_{as} Me
1457		2.62	11.35	δ CH ₂
1456	1454 w	0.01	13.96	δ_{as} Me
1417		2.62	1.25	ν Ph
1409	1411 s	17.76	0.27	δ_s Me
1389		3.29	1.68	δ_s Me
1387	1360 m	1.06	1.31	δ_s Me
1317	1330 w	0.10	1.71	ν Ph
1264	1267 m	28.16	2.65	ν_{as} CC ₃
1227	1226 w	49.47	120.15	ω CH ₂
1224		6.59	14.09	ν_{as} CC ₃
1205		2.47	8.46	δ CH
1188	1190 s	14.31	1.44	ν CX(X)
1176		2.33	28.01	τ CH ₂
1165		1.81	2.99	ρ Me
1099	1104 s	8.84	16.85	ν CX'(X)
1084		5.55	6.75	δ CH
1063		0.27	2.72	δ CH
1030	1028 w	0.00	4.15	ρ Me
1016	1017 w	2.01	4.03	ρ Me
996		4.92	0.35	δ CH
984		0.04	0.04	γ CH
970	964 vw	0.13	2.03	γ CH
939	942 vw	0.14	0.02	ρ Me
912		0.32	8.08	ρ Me
904	892 vw	1.34	9.38	ρ Me
850		13.73	1.40	δ Ph(X)
849	841 s	17.05	2.90	γ CH
834	829 vs	1.12	0.71	Ring breathing
821		0.79	10.33	ν_s CC ₃
782		0.28	13.56	ρ CH ₂
742	748 vw	0.57	3.26	γ CH
640	666 w	2.72	6.33	γ Ph
628		0.10	6.67	δ Ph
613	600 vs	35.75	66.52	ν_{as} CSeC
538	540 m	5.03	21.82	γ Ph(X)
505	513 s	10.53	2.22	ν CSe
499	500 w	4.20	1.06	δ Ph(X)
445		0.32	0.56	δ_{as} CC ₃
423		0.49	3.36	δ SeCN
422		4.61	3.40	γ SeCN
408		0.08	0.78	γ Ph

400		0.41	5.63	$\delta_{CX}(X)$
348		0.38	0.22	$\delta_{CX'}(X)$
345		0.31	1.09	$\delta_{as}CC_3$
329		0.01	0.05	δ_sCC_3
320		0.73	1.65	ρCC_3
286		0.86	0.81	ρCC_3
265		0.18	0.02	tor Me
241		0.15	1.80	tor Me
209		0.02	1.34	tor Me
191		0.73	0.14	$\gamma_{CX}(X)$
118		2.86	6.57	$\gamma_{CX'}(X)$
92		4.00	0.65	tor CC_3
52		0.09	4.33	tor $C\equiv N$
37		0.89	0.19	tor Ph
28		2.74	1.92	tor Ph
20		0.57	1.66	tor Ph

v, very; s, strong; w, weak; m, medium; br, broad; Me, methyl; Ph, phenyl; v, stretching; δ , in-plane deformation; γ , out-of-plane deformation; τ , twisting; ρ , rocking; ω , wagging; tor, torsional; (X), substituent sensitive; X' , selenocyanate group; subscript: as, antisymmetric; s, symmetric.



REFERENCES

1. B.S. Reddy, A. Rivenson, K. El-Bayoumy, P. Upadhyaya, B. Pittman and D.V. Rao, *J. Natl. Cancer Inst.*, **89**, 506 (1997).
2. J. Nayini, K. El-Bayoumy, S. Sugie, L.A. Cohen and B.S. Reddy, *Carcinogenesis*, **10**, 509 (1989).
3. B.S. Reddy, P. Upadhyaya, B. Simi and C.V. Rao, *Anticancer Res.*, **14**, 2509 (1994).
4. L.A. Jacob, B. Matos, C. Mostafa, J. Rodriguez and J.K. Tillotson, *Molecules*, **9**, 622 (2004).
5. H.E. Ganther, *Adv. Exp. Med. Biol.*, **492**, 119 (2001).
6. J.K. Tillotson, P. Upadhyaya and Z. RoaniZ, *Carcinogenesis*, **15**, 607 (1994).
7. H.F. Mayland, in: "Selenium in the Environment". W.T. Frankenberger, S. Benson : Eds.. Marcel Dekker Inc; New York, (1994).
8. K. El-Bayoumy, P. Upadhyaya, V. Date, O. Sohn, E.S. Fiala and B. Reddy, *Chem. Res. Toxicol.*, **4**, 560 (1991).

9. M.J.Frisch et al. Gaussian03, Gaussian Inc Wallingford CT (2004).
10. J.B. Foresman, in: E. Frisch, (Eds) "Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian", Gaussian; Pittsburg, PA, (1996).
11. P.Flukiger, H.P.Luthi, S.Portmann and J.Weber, MOLEKEL, 4.3, Swiss center for Scientific Computing, Manno, Switzerland (2000).
12. S.Portmann and H.P.Luthi, *Chimia*, **54**, 766 (2000).
13. N.P.G.Roeges, A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures, Wiley, New York (1994).
14. J.Coates, Encyclopedia of Analytical Chemistry, in: R.A.Meyers (Ed.) Interpretation of Infrared Spectrum, A Practical Approach, John Wiley and Sons Ltd. Chichester (2000).
15. D.L.Smith and V.I.Saunders, *Acta Crystallogr.* **37B**, 1807 (1981).
16. A.Manceau and D.L.Gallup, *Environ. Sci. Technol.* **31**, 968 (1997).
17. A.Sabatini and I.Bertinil, *Inorg. Chem.* **4(7)**, 959 (1965).
18. J.K.Grey, L.S.Butler and C.Reber, *Inorg. Chem.* **42(20)**, 6503 (2003).
19. N.B.Colthup, L.H. Daly, S.E.Wiberly, Introduction to Infrared and Raman Spectroscopy, ed. 3, Academic Press, Boston (1980).
20. G.Varsanyi, Assignments for vibrational Spectra of Seven Hundred Benzene Derivatives, Wiley, New York (1974).
21. P.Sykes, A Guide Book to Mechanism in Organic Chemistry, ed. 6, Pearson Education, India (2004).
22. K.R.Ambujakshan, V.S.Madhavan, H.T.Varghese, C.Y.Panicker, O.T.Arpaci, B.T.Gulbas and I.Yildiz, *Spectrochim. Acta Part A* doi. 10.1016 /j.saa. 2007. 04. 034.

(Received: 24 September 2007

Accepted: 13 January 2008

RJC-116)