

[104]

SEAT No. _____

No of Printed Pages: 03 + 04

SARDAR PATEL UNIVERSITY

M.Sc. Organic Chemistry

Semester – IV, External Examination

18th March ..., 2019, Monday

Time: 02:00 am - 05:00 pm

Spectroscopy-II [PS04CORC01]

[Total Marks – 70]

N.B. Figures to the right indicate full marks

Q.1 Answer the following multiple choice questions. [08]

- 1 Number of Br atoms are _____ in a compound showing abundance of M: M+2:M+4:M+6 as 1:4:6:4:1 in mass spectrum.

(a) 1 (b) 2 (c) 4 (d) 3

- 2 Carbonyl stretching of saturated aliphatic ketons falls in region _____ cm^{-1} .
(a) 1600-1700 (b) 1220-1250 (c) 1700-1800 (d) 1400-1450

- 3 In PMR spectrum of benzene _____ signals are obtained.
(a) 1 (b) 4 (c) 3 (d) 2

- 4 The HMBC spectra show _____.
(a) ^1J and ^3J connectivity (b) ^2J and ^2J connectivity
(c) ^2J and ^3J connectivity (d) ^3J and ^3J connectivity

- 5 In UV, the highest energy electronic transition is _____.
(a) $n \rightarrow \pi^*$ (b) $n \rightarrow \sigma^*$ (c) $\pi \rightarrow \pi^*$ (d) $\sigma \rightarrow \sigma^*$

- 6 In CI techniques for recording mass spectra, reagent gas used is generally _____.
(a) Argon (b) methane (c) helium (d) nitrogen

- 7 In ^{13}C -NMR, p-benzoquinone will give _____ signals.
(a) 1 (b) 4 (c) 3 (d) 2

- 8 At 300 MHz styrene gives _____ first order spectrum.
(a) AMX (b) AX (c) AX (d) ABM

Q.2 Answer the following questions. (ANY SEVEN)

[14]

- 1 Sketch the PMR spectrum for 1-nitropropane by taking approximate δ value for each signal and showing appropriate multiplicity.

- 2 Explain long range coupling with suitable example.

- 3 Write structures of shift reagents.

(P.T.O)

(1)

- 4 Explain McLafferty rearrangement takes place in alcohols.
- 5 Explain effect of conjugation on absorption of λ_{\max} in UV spectroscopy.
- 6 Explain Fermi resonance in IR spectroscopy.
- 7 Sketch the $^1\text{H} - ^{13}\text{C}$ HETCOR spectrum for ethyl chloride by taking approximate δ value for each signal.
- 8 Do the fragmentation of 2-pentanone based on McLafferty rearrangement.
- 9 Predict fragmentation pattern of diphenyl ether having molecular ion at $m/z = 170$.

Q.3

[A] Answer the following questions.

[06]

- I A compound gives following data in its mass spectrum, deduce structure of the compound.

m/z -	129	130	131	132	133	134	135	136	137
Relative Abundance	30	100	31	98	12	32	1.7	3.5	0.07

- II Explain chemical ionization method used in mass spectroscopy.

[B] Explain fragmentation pattern for aldehydes and acids using McLafferty rearrangement.

[06]

OR

[B] Answer the following questions.

- I Explain homolytic and heterolytic cleavage of single bond in mass spectroscopy.

II Derive, $m/z = B^2 r^2 / 2V$.

Q.4

[A] Answer the following questions.

[06]

- I Write short note on D_2O exchange in PMR.

II Define NOE, explain with suitable example of distinction of isomers using NOE-PMR spectra.

- [B] A compound with molecular formula $\text{C}_5\text{H}_{10}\text{O}$ shows following signals in its proton coupled ^{13}C -Spectra, interpret the data and assign the structure.

[06]

$\delta = 18$ (quartet, 6H), $\delta = 28$ (quartet, 3H)

$\delta = 42$ (doublet, 1H), $\delta = 212$ (singlet)

OR

- [B] Discuss the use of symmetry operations for checking the chemical shift equivalence between protons in PMR spectroscopy.

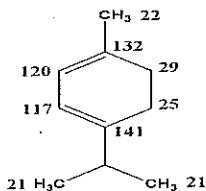
Q.5

[A] Do the ^{13}C -NMR chemical shift calculations for the following molecules.

[06]

- i) n-butanol
- ii) 3-me-pantane iii) P-Amino toluene

- [B] Sketch proton decoupled ^{13}C -NMR , DEPT-45, and DEPT-90 spectra for the [06] following compound.(use δ value assigned in the structure)



OR

- [B] An organic compound with molecular formula $\text{C}_9\text{H}_{10}\text{O}_2$ exhibits the following spectral data. Interpret deduce the structure of the compound.

IR: 1745, 1225, 749, 697 cm^{-1}

UV: λ_{max} 268, 264, 262, 257 nm

$^1\text{H-NMR}$: δ - 1.96(3H, S), 5.00(2H, S), 7.22(5H, S)

Q.6

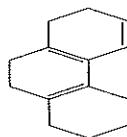
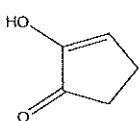
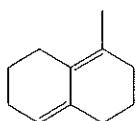
- [A] Answer the following questions. [06]

- I Write a short note on Fermi resonance.
II Explain short range couplings.

- [B] Calculate λ_{max} for the following compounds [06]

[1] [2]

[3]



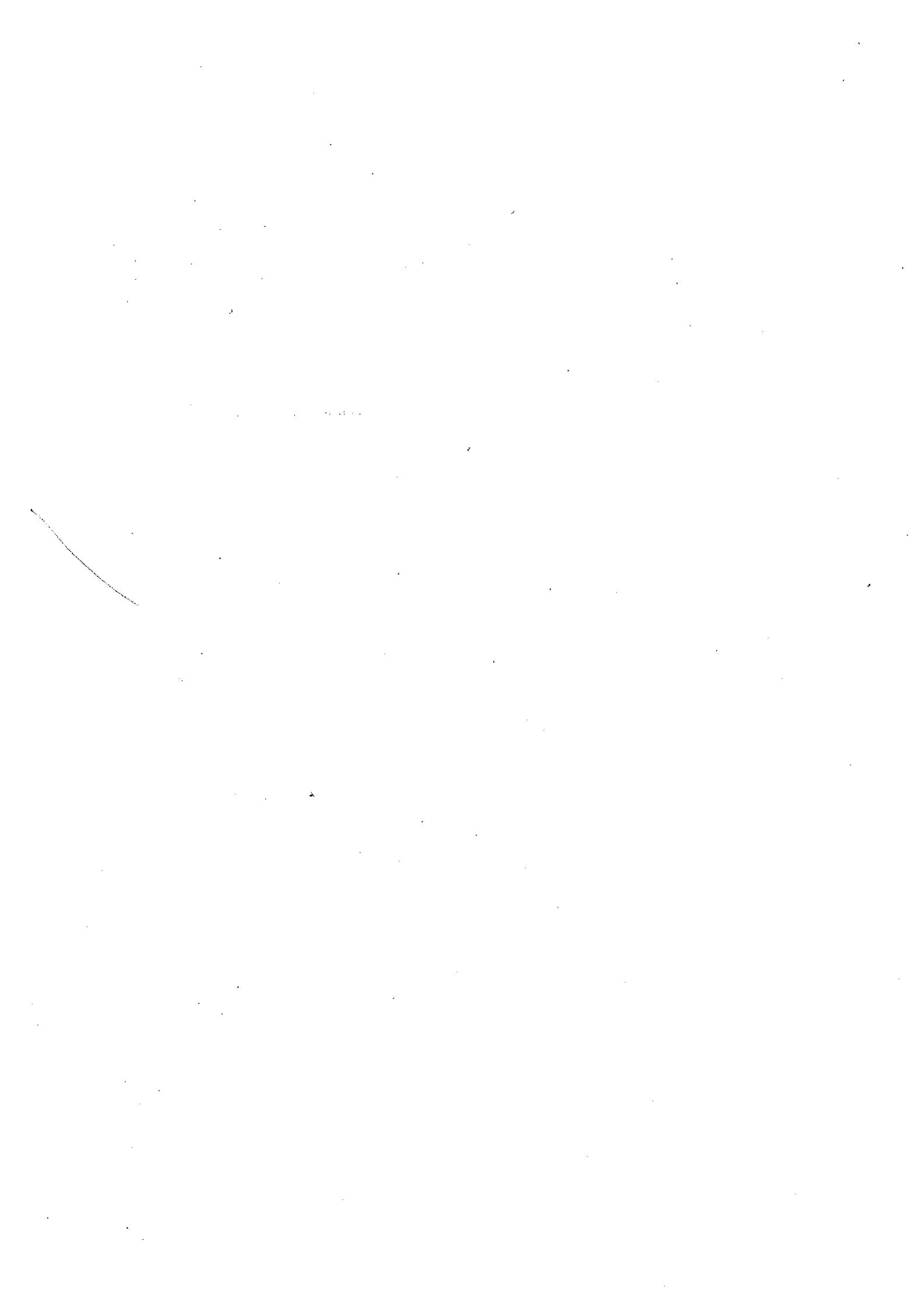
OR

[B]

- I Discuss important characteristic vibrations observed in nitriles.
II Calculate stretching frequency for C-C bond.

Answer : C_2H_2

— X —
③



[104]

SEAT No. _____

P504 CORC01

CHARACTERISTIC PROTON CHEMICAL SHIFTS

Type of proton		Chemical shift, ppm
Cyclopropane		8
Primary	RCH_3	0.2
Secondary	R_2CH_2	0.9
Tertiary	R_3CH	1.3
Vinylic	$\text{C}=\text{C}-\text{H}$	4.6-5.9
Acetylenic	$\text{C}\equiv\text{C}-\text{H}$	1-3
Aromatic	$\text{Ar}-\text{H}$	6-8.5
Benzyllic	$\text{Ar}-\text{C}-\text{H}$	2.2-3
Allylic	$\text{C}=\text{C}-\text{CH}_3$	1.7
Fluorides	$\text{HC}-\text{F}$	4-4.5
Chlorides	$\text{HC}-\text{Cl}$	3-4
Iodides	$\text{HC}-\text{I}$	2.5-4
Alcohols	$\text{HC}-\text{OH}$	2-4
Ethers	$\text{HC}-\text{OR}$	3.3-4
Esters	$\text{RCOO}-\text{CH}_3$	3.7-4.1
Acids	$\text{HC}-\text{COOR}$	2-2.2
Carboxylic compounds	$\text{HC}-\text{COOH}$	2-2.6
Aldehydic	$\text{HC}-\text{C=O}$	2-2.7
Hydroxyllic	$\text{R}-\text{CHO}$	9-10
Phenolic	$\text{Ar}-\text{OH}$	1-5.5
Enolic	$\text{C}=\text{C}-\text{OH}$	4-12
Carboxylic	RCOOH	15-17
Amino	RNH_2	10.5-12
		1-5

Characteristic Infrared Absorption Frequencies

Bond	Compound type	Frequency range, cm^{-1}
C-H	Alkanes	2850-2960 1350-1470
C-H	Alkenes	3020-3080 (m) 675-1000
C-H	Aromatic rings	3000-3100 (m) 675-870
C-H	Alkynes	3300
C=C	Alkenes	1640-1680 (v)
C=C	Alkynes	2100-2260 (v)
C-O	Aromatic rings	1500, 1600 (v)
C=O	Alcohols, ethers, carboxylic acids, esters	1080-1300
C=O	Aldehydes, ketones, carboxylic acids, esters	1690-1760
O-H	Monomeric alcohols, phenols Hydrogen bonded alcohols, phenols Carboxylic acids	3610-3640 (v) 3200-3600 (broad) 2500-3000 (broad)
N-H	Amines	3300-3500 (m)
C-N	Amines	1180-1360
C≡N	Nitriles	2210-2260 (v)
-NO ₂	Nitro compounds	1515-1560 1345-1385

(1)

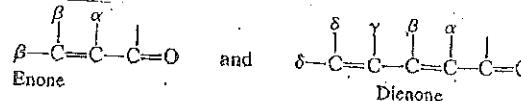
Characteristic absorption for dienes

Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5
Polar groupings: OAc	+0
OAlk	+6
SAIk	+30
Cl, Br	+5
N(Alk) ₂	+60
Solvent correction ^b	+0
$\lambda_{\text{calc}} = \text{Total}$	

Characteristic absorption for substituted benzene derivatives

ArCOR/ArCHO/ArCO ₂ H/ArCO ₂ R	$\lambda_{\text{max}}^{\text{ECDH}}$ (nm)
Parent chromophore: Ar = C ₆ H ₅	
G = Alkyl or ring residue, (e.g., ArCOR)	246
G = H, (ArCHO)	250
G = OH, OAlk, (ArCO ₂ H and ArCO ₂ R)	230
Increment for each substituent on Ar:	
—Alkyl or ring residue	o-, m- +3 p- +10 o-, m- +7 p- +25 o- +11 m- +20 p- +78 ^a o-, m- +0
—OH, —OCH ₃ , —OAlk	
—O ⁻ (oxyanion)	
—Cl	p- +10 o-, m- +2 p- +15 o-, m- +13 p- +58 o-, m- +20
—Br	
—NH ₂	
—NHCOCH ₃	
—NHCH ₃	
—N(CH ₃) ₂	

Characteristic absorption for α, β -unsaturated carbonyl compounds



Base values	
Acyclic α,β -unsaturated ketones	(nm) 215
Six-membered cyclic α,β -unsaturated ketones	215
Five-membered cyclic α,β -unsaturated ketones	215
α,β -Unsaturated aldehydes	202 210
α,β -Unsaturated carboxylic acids and esters	195

Increments for

Double bond extending conjugation	+30
Alkyl group, ring residue	α +10 β +12 γ and higher +18
Polar groupings: —OH	α +35 β +30 δ +50 —OAc α, β, δ +6 —OMe α +35 β +30 γ +17 δ +31 —SAIk β +85 —Cl α +15 β +12 —Br α +25 β +30 —NR ₂ β +95
Exocyclic double bond	+5
Homodiene component ^a	+39

¹³C shifts for terminal and internal systems

Y	Terminal		Internal		γ	
			β			
	Terminal	Internal	Terminal	Internal		
CH ₃	+ 9	+ 6	+ 10	+ 8	-2	
CH=CH ₂	+ 20		+ 6		-0.5	
C≡CH	+ 4.5		+ 5.5		-3.5	
COOH	+ 21	+ 16	+ 3	+ 2	-2	
COO ⁻	+ 25	+ 20	+ 5	+ 3	-2	
COOR	+ 20	+ 17	+ 3	+ 2	-2	
COCl	+ 33	+ 26		+ 2		
CONH ₂	+ 22		+ 2.5		-0.5	
COR	+ 30	+ 24	+ 1	+ 1	-2	
CNO	+ 31		0		-2	
Piessyl	+ 23	+ 17	+ 9	+ 7	-2	
OH	+ 45	+ 41	+ 10	+ 8	-5	
OR	+ 58	+ 31	+ 8	+ 5	-4	
OCOR	+ 51	+ 45	+ 6	+ 5	-3	
NH ₂	+ 29	+ 24	+ 11	+ 10	-5	
NH ₃ ⁺	+ 26	+ 24	+ 8	+ 6	-5	
NHR	+ 37	+ 31	+ 8	+ 6	-4	
NR ₃	+ 42		+ 6		-3	
NR ₂ ⁺	+ 31		+ 5		-7	
NO ₂	+ 63	+ 57	+ 4	+ 4		
CN	+ 4	+ 1	+ 3	+ 3	-3	
SH	+ 11	+ 11	+ 12	+ 11	-4	
SR	+ 20		+ 7		-3	
F	+ 68	+ 63	+ 9	+ 6	-4	
Cl	+ 31	+ 32	+ 11	+ 10	-4	
Br	+ 20	+ 25	+ 11	+ 10	-3	
I	- 6	+ 4	+ 11	+ 12	-1	

¹³C Shifts for some linear and branched chain alkanes

Component	C1	C2	C3	C4	C5
Methane	-2.3				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isobutane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	20.1	30.6	36.9	8.9	
3-Methylpentane	11.3	23.5	36.9	(18.4)	3-(CH ₃)
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Triisopropylpropane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6)	3-(CH ₃)

(P.T.O)

(3)

¹³C shifts for substituted benzenes
Base value for benzene is 128.5 ppm

Substituent	C1 (Aromatic)	C2			C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27	C28	C29	C30	C31	C32	C33	C34	C35	C36	C37	C38	C39	C40	C41	C42	C43	C44	C45	C46	C47	C48	C49	C50	C51	C52	C53	C54	C55	C56	C57	C58	C59	C60	C61	C62	C63	C64	C65	C66	C67	C68	C69	C70	C71	C72	C73	C74	C75	C76	C77	C78	C79	C80	C81	C82	C83	C84	C85	C86	C87	C88	C89	C90	C91	C92	C93	C94	C95	C96	C97	C98	C99	C100	C101	C102	C103	C104	C105	C106	C107	C108	C109	C110	C111	C112	C113	C114	C115	C116	C117	C118	C119	C120	C121	C122	C123	C124	C125	C126	C127	C128	C129	C130	C131	C132	C133	C134	C135	C136	C137	C138	C139	C140	C141	C142	C143	C144	C145	C146	C147	C148	C149	C150	C151	C152	C153	C154	C155	C156	C157	C158	C159	C160	C161	C162	C163	C164	C165	C166	C167	C168	C169	C170	C171	C172	C173	C174	C175	C176	C177	C178	C179	C180	C181	C182	C183	C184	C185	C186	C187	C188	C189	C190	C191	C192	C193	C194	C195	C196	C197	C198	C199	C200	C201	C202	C203	C204	C205	C206	C207	C208	C209	C210	C211	C212	C213	C214	C215	C216	C217	C218	C219	C220	C221	C222	C223	C224	C225	C226	C227	C228	C229	C230	C231	C232	C233	C234	C235	C236	C237	C238	C239	C240	C241	C242	C243	C244	C245	C246	C247	C248	C249	C250	C251	C252	C253	C254	C255	C256	C257	C258	C259	C260	C261	C262	C263	C264	C265	C266	C267	C268	C269	C270	C271	C272	C273	C274	C275	C276	C277	C278	C279	C280	C281	C282	C283	C284	C285	C286	C287	C288	C289	C290	C291	C292	C293	C294	C295	C296	C297	C298	C299	C300	C301	C302	C303	C304	C305	C306	C307	C308	C309	C310	C311	C312	C313	C314	C315	C316	C317	C318	C319	C320	C321	C322	C323	C324	C325	C326	C327	C328	C329	C330	C331	C332	C333	C334	C335	C336	C337	C338	C339	C340	C341	C342	C343	C344	C345	C346	C347	C348	C349	C350	C351	C352	C353	C354	C355	C356	C357	C358	C359	C360	C361	C362	C363	C364	C365	C366	C367	C368	C369	C370	C371	C372	C373	C374	C375	C376	C377	C378	C379	C380	C381	C382	C383	C384	C385	C386	C387	C388	C389	C390	C391	C392	C393	C394	C395	C396	C397	C398	C399	C400	C401	C402	C403	C404	C405	C406	C407	C408	C409	C410	C411	C412	C413	C414	C415	C416	C417	C418	C419	C420	C421	C422	C423	C424	C425	C426	C427	C428	C429	C430	C431	C432	C433	C434	C435	C436	C437	C438	C439	C440	C441	C442	C443	C444	C445	C446	C447	C448	C449	C450	C451	C452	C453	C454	C455	C456	C457	C458	C459	C460	C461	C462	C463	C464	C465	C466	C467	C468	C469	C470	C471	C472	C473	C474	C475	C476	C477	C478	C479	C480	C481	C482	C483	C484	C485	C486	C487	C488	C489	C490	C491	C492	C493	C494	C495	C496	C497	C498	C499	C500	C501	C502	C503	C504	C505	C506	C507	C508	C509	C510	C511	C512	C513	C514	C515	C516	C517	C518	C519	C520	C521	C522	C523	C524	C525	C526	C527	C528	C529	C530	C531	C532	C533	C534	C535	C536	C537	C538	C539	C540	C541	C542	C543	C544	C545	C546	C547	C548	C549	C550	C551	C552	C553	C554	C555	C556	C557	C558	C559	C560	C561	C562	C563	C564	C565	C566	C567	C568	C569	C570	C571	C572	C573	C574	C575	C576	C577	C578	C579	C580	C581	C582	C583	C584	C585	C586	C587	C588	C589	C590	C591	C592	C593	C594	C595	C596	C597	C598	C599	C600	C601	C602	C603	C604	C605	C606	C607	C608	C609	C610	C611	C612	C613	C614	C615	C616	C617	C618	C619	C620	C621	C622	C623	C624	C625	C626	C627	C628	C629	C630	C631	C632	C633	C634	C635	C636	C637	C638	C639	C640	C641	C642	C643	C644	C645	C646	C647	C648	C649	C650	C651	C652	C653	C654	C655	C656	C657	C658	C659	C660	C661	C662	C663	C664	C665	C666	C667	C668	C669	C670	C671	C672	C673	C674	C675	C676	C677	C678	C679	C680	C681	C682	C683	C684	C685	C686	C687	C688	C689	C690	C691	C692	C693	C694	C695	C696	C697	C698	C699	C700	C701	C702	C703	C704	C705	C706	C707	C708	C709	C710	C711	C712	C713	C714	C715	C716	C717	C718	C719	C720	C721	C722	C723	C724	C725	C726	C727	C728	C729	C730	C731	C732	C733	C734	C735	C736	C737	C738	C739	C740	C741	C742	C743	C744	C745	C746	C747	C748	C749	C750	C751	C752	C753	C754	C755	C756	C757	C758	C759	C760	C761	C762	C763	C764	C765	C766	C767	C768	C769	C770	C771	C772	C773	C774	C775	C776	C777	C778	C779	C780	C781	C782	C783	C784	C785	C786	C787	C788	C789	C790	C791	C792	C793	C794	C795	C796	C797	C798	C799	C800	C801	C802	C803	C804	C805	C806	C807	C808	C809	C810	C811	C812	C813	C814	C815	C816	C817	C818	C819	C820	C821	C822	C823	C824	C825	C826	C827	C828	C829	C830	C831	C832	C833	C834	C835	C836	C837	C838	C839	C840	C841	C842	C843	C844	C845	C846	C847	C848	C849	C850	C851	C852	C853	C854	C855	C856	C857	C858	C859	C860	C861	C862	C863	C864	C865	C866	C867	C868	C869	C870	C871	C872	C873	C874	C875	C876	C877	C878	C879	C880	C881	C882	C883	C884	C885	C886	C887	C888	C889	C890	C891	C892	C893	C894	C895	C896	C897	C898	C899	C900	C901	C902	C903	C904	C905	C906	C907	C908	C909	C910	C911	C912	C913	C914	C915	C916	C917	C918	C919	C920	C921	C922	C923	C924	C925	C926	C927	C928	C929	C930	C931	C932	C933	C93