Monatshefte für Chemie 108, 799—802 (1977)

Monatshefte für Chemie

Chalcones XVI: Infrared Spectral Studies of Phenanthryl Chalcones

By

Shyam Sunder Misra*

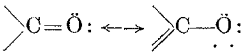
Department of Chemistry,
Harcourt Butler Technological Institute, Kanpur, India

(Received May 12, 1976)

IR absorption spectra of ten phenanthryl chalcones have been studied with a view to see the effect on stretching frequencies of α,β-unsaturated carbonyl group when conjugated to the phenanthryl nucleus.

Infrared absorption spectra of chalcone analogues have been reported by several workers[1, 2, 6, 10], but little attention has been paid to the effect of polynuclear groups on the stretching frequency of α,β-unsaturated carbonyl group. The present work has, therefore, been undertaken to gain more information about the spectroscopic characteristics of phenanthryl chalcones, which may lead to interesting generalisations on the structure—spectra correlations.

The infrared absorption spectra of a simple open chain ketone, undisturbed by neighbouring groups, exhibits[7] absorption in the range 1720—1706 cm^{-1}, acetophenone[9] gives strong peak for ν_{max} C=O group at 1686 cm^{-1}, isophorone (having olefinic conjugation with CO group) shows[8] stretching frequency for $>$CO group at 1672 cm^{-1} and benzalacetophenone has a strong band for α,β-unsaturated keto group at 1667 cm^{-1}. In present case of phenanthryl chalcones the frequencies for the said group fall in the range of 1655—1684 cm^{-1}. Thus a gradual lowering in stretching frequency of ketonic group is observed. These findings clearly indicate that the conjugation of α,β-unsaturated carbonyl group with phenanthryl nucleus results in lowering of stretching frequency. This behaviour may possibly be due to increase in length of olefinic conjugation on either side of the —CH=CH—CO-group and/or different canonical forms of the $>C=O$ group as illustrated below



$$>C=\ddot{O}: \longleftrightarrow >\overset{+}{C}—\underset{\cdot\cdot}{\ddot{O}}:$$

---

[*] Present address: Department of Chemistry, Feroze Gandhi Post-Graduate College, Rae-Bareli 229001.

Table 1. Ar—CH=CH—CO—Ar′

Compd. No.	Ar	Ar′
1	3-nitrophenyl	2-phenanthryl
2	4-dimethylaminophenyl	2-phenanthryl
3	2-bromo-4,5-dimethoxyphenyl	2-phenanthryl
4	2-bromophenyl	3-phenanthryl
5	2,4-dihydroxyphenyl	3-phenanthryl
6	4-dimethylaminophenyl	3-phenanthryl
7	1-naphthyl	3-phenanthryl
8	3-bromo-4-hydroxy-5-methoxyphenyl	3-phenanthryl
9	2,6-dichlorophenyl	3-phenanthryl
10	2-bromo-4,5-dimethoxyphenyl	3-phenanthryl

Table 2. *Infrared Absorption*

cm^{-1}	Mode of vibration	Observed			
		1*	**2***	**3***	**4***
3100–3000	ν CH (Aromatic)	3040	3058	3049	3058
3000	ν CH (Olefin)	3003	3012	3003	3012
2870–2855			2860		
1685–1665	ν C=O	1664	1684	1678	1661
1647–1621	ν C=C	1653	1645, 1623	1642, 1629	1650, 1623
1650–1600	Skeletal Vibn.	1608, 1597	1645, 1631	1642, 1618	1650, 1623
1630–1575	Condensed	1592, 1570	1527, 1495	1595, 1504	1610, 1600
1525–1450	Systems	1513		1462	1575, 1466
1600–1500	Phenylalkene	1592, 1570	1597, 1572	1575, 1550	1590, 1560
1548–1508	ν asy NO_2	1534			
1356–1340	ν sy NO_2	1355			
2850	ν_s CH_3 (*Ar*—OCH_3)			2833	
1250	ν_{as} (C=C—**O**—C)			1250	
1460	δ CH			1453	
1616–1598					1610, 1600
1581–1573	Benzene ring				1575, 1466
1510–1460	Vibn. (o-disubs.)				
1457–1427					1439
1410–1310	δ OH (Phenol)				
1260–1180	ν C—O—(Phenol)				
1292–1272	ν C—C—C	1272	1266	1285, 1266	1284, 1271
1286–1252					
1164–1156	Benzene ring				1284 1271,
1139–1111	Vibn. (o-disub.)				1163, 1031
1040–1022					1027
1175–1125	δ CH Substituted	1175, 1167	1188, 1147	1195, 1174	1190, 1186
1110–1070	Phenyl	1145, 1095	1105, 1003	1167, 1144	1175, 1053
1070–1000		1052, 1001		1099, 1001	1000
1057–1034	ν *Ar*—Cl (o-)				
1042–1028	ν *Ar*—Br (o-)			1031	1031
980–965	ϑ CH	985, 978	976, 959	982, 978	985, 972
Below 900	ϑ CH		895, 835	870	867

---

* Compound numbers correspond to those reported in Table 1.

ν = Stretching; δ = Bending (in-plane), ϑ = Bending (out of plane).

In addition to this an upward frequency shift is also observed as in case of compound nos. **2**, **3**, **5**, and **8**. This may be attributed to the presence of strong electronegative groups such as chloro, bromo, p-dimethylamino, etc. These functionals with their strong electron attracting power diminish the polar character of the carbonyl group link and consequently raise the stretching frequency.

Experimental

The chalcones under study were derived[3, 4] from 2- and 3-acetyl phenanthrenes and benzaldehydes and were repeatedly crystallised from different organic solvents. The final purity was checked by thin layer chro-

Bands of Phenanthryl Chalcones

bands, cm^{-1} 5*	6*	7*	8*	9*	10*
3077	3049	3058	3049	3049	3049
3012	3012 2857	3012	3003	3003	3003
1681	1655	1661	1678	1664	1658
1653	1623	1634	1608	1616	1629
1610, 1511	1610, 1603	1613, 1600	1595, 1508	1616, 1553	1608, 1561
1486, 1449	1575, 1527 1481	1575, 1511 1504	1490, 1458	1508	1499, 1462
1565, 1506	1575, 1560	1600, 1553	1595	1553, 1508	1590, 1499
			2833		2857
			1258		1261, 1242
			1458		1462
1359			1420, 1360		
1259, 1242			1258, 1242		
1279	1282	1282	1280	1287	1299, 1284
1148, 1105	1185, 1172	1190, 1174	1174, 1140	1144, 1094	1190, 1166
1040, 1020	1099, 1059	1147, 1096	1133, 1101	1050, 1013	1149, 1096
	1038, 1055	1054, 1009	1045		1027, 1018
				1050, 1038	
			1050, 1038		1055, 1038
968, 957	985	976	968	976	978
860, 849	843	844	867, 859 844	844	866

matography on silica gel-G using petroleum ether (b.p. 40–60°) and ethyl acetate (5 : 1) as developer solvents[5] (Table 1).

Infrared absorption spectra were recorded in $CHCl_3$ solution, 0.1 mm thickness, in the range 4000–650 cm^{-1} on Beckman model IR-7 precision prism grating spectrophotometer. The region 825–750 cm^{-1} has been obscured due to $CHCl_3$ absorption and the assignment of various bands are reported in Table 2.

References

[1] *A. Nayak, P. L. Nayak, B. K. Sabata*, and *M. K. Rout*, J. Indian Chem. Soc. **41**, 507 (1964).
[2] *D. N. Dhar* and *V. P. Gupta*, Indian J. Chem. **9**, 818 (1971).
[3] *S. S. Misra*, J. Indian Chem. Soc. **50**, 335 (1973).
[4] *S. S. Misra* and *Bhola Nath*, Indian J. Appl. Chem. **34**, 260 (1971).
[5] *D. N. Dhar* and *S. S. Misra*, J. Chromatog. **69**, 416 (1972).
[6] *N. L. Silver* and *D. W. Boykin*, Jr., J. Org. Chem. **35**, 759 (1970).
[7] *H. McCombie, B. C. Saunders*, and *G. J. Stacey*, J. Chem. Soc. **1945**, 380.
[8] *T. Rasmussen* and *J. Tunnicliff*, J. Amer. Chem. Soc. **71**, 1068 (1949).
[9] *W. Thompson* and *N. Torkington*, J. Chem. Soc. **1945**, 640.
[10] *S. S. Misra*, Mh. Chem. **104**, 11 (1973).

Correspondence and reprints:
Dr. S. S. Misra
P. O. Bichhwan
Dist. Mainpuri 205 267
India