Polarities and Hydrogen-bonding Abilities of the Aromatic Derivatives of Cyclohex-2-enone

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The relative basicities of 3-aryl-5-phenylcyclohex-2-enones have been determined by i.r. spectroscopy from the shifts of the stretching frequency of the hydroxy-group of phenol hydrogen-bonded with these ketones and from the $\nu_{C=O}$ values (in KBr, CCl_4, and $CHCl_3$) together with the dipole moments (in benzene). The values are discussed and compared with those of arylideneacetones having analogous conjugated systems. It is shown that the fixed *s-trans*-configuration of cyclohexenone derivatives causes their high polarities and basicities. Correlation analysis has been performed and it is found that the rigid π-system of cyclohexenone possesses a substantially better transmission of electronic influence in comparison with carbonyl compounds with an open-chain structure.

It is known [1,2] that the conformation of $\alpha\beta$-unsaturated ketones determines the majority of their physicochemical properties mainly because of its effect on the mutual orientation of the polarities of the attached groups. For this reason, there is special interest in the investigation of the basicity and polarity of carbonyl compounds which, due to the fixed structure of the propenone unit, do not have the conformational uncertainty found with acyclic compounds.

In the present study, the properties of 3-aryl-5-phenylcyclohex-2-enones possessing fixed *s-trans*-conjugated chains have been investigated. The shifts of the stretching frequency of the hydroxy-group of phenol ($\Delta\nu_{O-H}$) in ketone–phenol–CCl_4 systems, the characteristic stretching frequency of the carbonyl group ($\nu_{C=O}$) in the solid state (KBr pellets) and in CCl_4 and $CHCl_3$ solutions, and the dipole moments (μ) of these compounds were measured. Analogous data have been reported [3,4] for a group of labile *s-trans*-conformers of arylideneacetones of similar conjugation.

EXPERIMENTAL

M.p.s and physical data for the compounds studied are given in Table 1.

I.r. spectra were recorded with a UR-20 spectrometer. The pellets used for the solid state measurements contained 1—2 mg of ketone per 100 mg of KBr. For the other measurements a constant path-length (1 mm) cell was used. The temperature of the cell was regulated at 30.0 ± 0.5 °C. Spectroscopic grade CCl_4 and $CHCl_3$ were dried over molecular sieves and stored in a dry box where all solutions were prepared. The ketone concentrations were *ca.* 0.01M for the $\nu_{C=O}$ and 0.1M for the $\Delta\nu_{O-H}$ studies and the starting phenol concentration was 0.02M. The solutions containing phenol and base typically yielded spectra in which the broad band due to the hydrogen bonded hydroxy-group did not overlap with the monomeric band for any of the compounds studied. The maxima for the hydrogen-bonded hydroxy stretching bands were determined by a triangulation procedure. The intersection of the lines that best fit the sides of the band was taken to be the centre of the peak.

Dipole moments (μ_{obs}) were measured by the Hedestrand procedure [5] in benzene at 25 °C. For $\mu_{calc.}$ the standard group moment values [6] were used, except that $\mu_{C=O}$ was taken as equal to μ for cyclohex-2-enone (3.6 D [7]). Each $\nu_{C=O}$ and $\mu_{obs.}$ entry is the average of at least two separate

TABLE 1

Experimental data

				$p\text{-R}^1\text{C}_6\text{H}_4\cdot\overbrace{\text{C:CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}}^{\text{CH}_2}\cdot\text{C}_6\text{H}_4\text{R}^2\text{-}p$						$p\text{-R}^1\text{C}_6\text{H}_4\cdot\text{CH:CH}\cdot\text{COMe}$	$p\text{-R}^1\text{C}_6\text{H}_4\cdot\text{CH:}\overbrace{\text{C}\cdot\text{CO}\cdot\text{CH}_2}^{[\text{CH}_2]_3}$
				$\Delta\nu_{OH}$/	$\nu_{C=O}/cm^{-1}$			μ/D			
R^1	R^2	No.	M.p. (°C)	cm^{-1}	KBr	CCl_4	$CHCl_3$	obs.	calc.	μ/D ‖	μ/D ‖
H	H	(I)	89—90 *	247 ± 1	1 663	1 673	1 659	3.57 §	3.60	3.31	3.14
CH_3	H	(II)	106.5—107.5 †	251 ± 1	1 661	1 673	1 658	4.00	3.82	3.63	
OCH_3	H	(III)	107—108 ‡	255 ± 1	1 658	1 671	1 656	4.21	4.01	3.19	
$N(CH_3)_2$	H	(IV)	167	285 ± 2	1 650	1 660	1 644	5.54	4.53	5.30	
Cl	H	(V)	98—99 §	239 ± 2	1 662	1 675	1 662	3.15 §	3.12	2.63	2.75
Br	H	(VI)	117	236 ± 2	1 661	1 676	1 662	3.22	3.13		2.89
NO_2	H	(VII)	130	203 ± 1	1 667	1 685	1 672	3.68	3.82	3.45	
OCH_3	OCH_3	(VIII)	110—111	261 ± 3	1 656	1 669	1 654				
		(IX) ¶	64	253 ± 2	1 661	1 673	1 658	3.64	3.60		

* Literature values of the m.p. vary between 80 and 90 °C. The value 89—90 °C has been reported by D. Nasipuri, S. R. R. Chouldhury, and A. Bhattacharya, *J.C.S. Perkin I*, 1973, 1451; H. E. Zimmerman, D. F. Juars, J. M. McCall, and B. Schroder, *J. Amer. Chem. Soc.*, 1971, **93**, 3662. † Lit. m.p. 103—104 °C (A. D. Petrov, and L. I. Antzus, *Ber.*, 1933, **66B**, 420). ‡ Lit. m.p. 103—104 °C [R. G. Grict, G.P. 1,921,348 (*Chem. Abs.*, 1970, **72**, P54,991d)]. § Lit. m.p. 95 °C, $\mu_{obs.}$ 3.4 D for (V); $\mu_{obs.}$ 3.9 D for (I) (A. Y. Meyer and E. D. Bergmann, *Israel J. Chem.*, 1968, **6**, 735). ¶ 3-Phenylcyclohex-2-enone, lit. m.p. 64 °C (S. M. Abdullah, *J. Indian Chem. Soc.*, 1935, **12**, 62). ‖ The values of μ were taken from O. A. Osipov, V. I. Minkin, and A. D. Garnovskiy, ' Handbook of Dipole Moments,' Vysshaya shkola, Moscow, 1971, 3rd edn.

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determinations. The $\Delta\nu_{O-H}$ values were calculated statistically from 7—8 independent measurements.

DISCUSSION

The electric dipole moment of an organic compound is one of the most direct measures of the total polarization of the ground state of the molecule. For that reason, it is interesting to use that quantity for analysis of the cyclohex-2-enone derivatives.

The values of $\mu_{obs.}$ for cyclohex-2-enone (3.62 D[7]), 3-phenyl-(3.64 D), and 3,5-diphenyl-cyclohex-2-enone (3.57 D) are very close. Apparently, the effect of the aryl group on the total polarization of the molecule is very small. On the other hand, μ for the cyclohexenone ring is larger than expected based on an enone model. Since the directions of the carbonyl group and the adjacent double bond polarizations are parallel, the calculated moment should be the sum of $\mu_{C=O}$ (2.7 D) and $\mu_{C=C}$ (0.4 D[6]), *i.e.*, $\mu_{calc.}$ 3.1 D. The difference between $\mu_{obs.}$ and $\mu_{calc.}$ is large enough (*ca.* 0.5 D) to indicate that there is interaction between these groups. In our calculation of μ for compounds (I)—(VII) a correction for this interaction has been made and the $\mu_{calc.}$ values obtained are in good agreement with $\mu_{obs.}$ (see Table 1). An exception is ketone (IV) in which the strongly electron-donating dimethylamino-group exerts much influence on the carbonyl group, creating an additional interaction moment.

TABLE 2

Data for correlation analysis

Set	No.	Equation	m *	s_0 †	r *,‡
a	(1)	$\Delta\nu^{R}_{O-H} = \Delta\nu^{H-H}_{O} + m\sigma$	$m = -48.8\ (-44.4)$	4.9	0.99 (0.98)
	(2)	$\Delta\nu^{R}_{O-H} = \Delta\nu^{H}_{O-H} + m\sigma^{+}$	$m = -29.5\ (-30.9)$	7.6	0.96 (0.94)
	(3)	$\Delta\nu^{R}_{O-H} = \Delta\nu^{H}_{O-H} + m_o\sigma^{o} + m_R\sigma_R^{+}$	$m_o = -45.1\ (-39.7)$ $m_R = -13.2\ (-8.9)$	3 8	0 99 (0.96)
	(4)	$\Delta\nu^{R}_{O-H} = \Delta\nu^{H}_{O-H} + m_f F + m_r R$	$m_f = -27.9\ (-25.0)$ $m_r = -48.5\ (-44.3)$	4.7	0.98 (0.94)
b	(1)	$\nu^{R}_{C=O} = \nu^{H}_{C=O} + m\sigma$	$m = 14.6$	1.5	0.98
	(2)	$\nu^{R}_{C=O} = \nu^{H}_{C=O} + m\sigma^{+}$	$m = 9.0$	1.9	0.97
	(3)	$\nu^{R}_{C=O} = \nu^{H}_{C=O} + m_o\sigma^{o} + m_R\sigma_R^{+}$	$m_o = 11.3\ (6.7)$ $m_R = 6.1\ (5.1)$	1.7	0.98 (0.97)
	(4)	$\nu^{R}_{C=O} = \nu^{H}_{C=O} + m_f F + m_r R$	$m_f = 7.0\ (5.0)$ $m_r = 13.3\ (10.2)$	1.6	0.97 (0.95)

* Data in parentheses are for corresponding *s-trans*-arylideneacetones. † Standard deviation. ‡ Correlation coefficient.

The values of $\mu_{obs.}$ presented in Table 1 show that the polarizations of cyclohexenone derivatives are considerably greater than those of the π-analogue derivatives of benzylideneacetone and 2-benzylidenecyclohexanone. The arylideneacetones exist as *s-trans-* and *s-cis*-rotamer mixtures [2-4] while 2-arylidenecyclohexanones have only the *s-cis*-form. It may be concluded that the conformation is the principal factor causing the difference in μ for related compounds in those series. The conformation also determines the polarity of the carbonyl group for each rotamer.

We now turn to the polarities of some compounds which have the same conformation. I.r. spectral measurements are especially helpful for such investigations. The $\nu_{C=O}$ values in different media are shown in Table 1. It is known [8] that in going from CCl_4 solution to the solid dispersion in KBr the value of $\nu_{C=O}$ decreases because of a change in the dipole–dipole interaction. A stronger interaction increases $\Delta\nu_{C=O}$. In the present case, the large $\Delta\nu_{C=O}$ values are due to the high polarity of the carbonyl group as confirmed by the μ values. Because of that high carbonyl group polarity the difference between $\nu_{C=O}$ in CCl_4 and $CHCl_3$ is also large (13—16 cm^{-1}).

The changes in $\nu_{C=O}$ due to the electronic influence of the R^1 substituents (see Table 1) are greater than the error of the method and reflect the different carbonyl group polarities that result. Despite the long distance (three single bonds) over which it acts the influence of the aromatic ring upon the carbonyl group is observable. The negative inductive effect of the phenyl group is shown by comparing the values of $\nu_{C=O}$, and especially, $\Delta\nu_{O-H}$ for compounds (I) and (IX) and the donor effect of the *p*-methoxyphenyl group is similarly seen by comparison of the values for (III) and (VIII).

The $\Delta\nu_{O-H}$ values are the most sensitive indications of the carbonyl polarity. The formation of the hydrogen-bonded complex causes a small displacement of the ketone from its ground state.

Comparison of our values of $\Delta\nu_{O-H}$ with those found for a series of arylideneacetone *s-trans*-rotamers [4] shows that the latter are smaller. The carbon skeleton of a cyclic molecule is more rigid than that of an open-chain aliphatic conjugative bond system, *e.g.*, benzylideneacetone which exists as a mixture of conformers. Briegleb–Stuart models show that the conjugative bond system of the cyclohexenone derivatives (I)—(VII) is almost planar, a conclusion reached earlier by others.[7,9] This is surely the dominant factor causing the high polarity of the unsaturated cyclic ketones of *s-trans*-configuration.

The transmission of electronic influence is a matter of interest here. As we have pointed out in our preliminary communications,[10] rigidity of the conjugative chain simplifies the consideration of electronic interaction because it removes conformational uncertainty.

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We have been able to make a quantitative estimate of the influence of substituents in the 3-phenyl ring upon the $\nu_{C=O}$ and $\Delta\nu_{O-H}$ values by carrying out a comprehensive correlation analysis employing both the monoparameter equations of Hammett (1) [11] and Brown (2) [11] and the two-parameters equations of Yukawa–Tsuno (3) [11] and Swain–Lupton (4).[12] The results of the analysis are given in Table 2. The data in parentheses were obtained earlier [3,4] for a series of analogous *s-trans*-arylideneacetones. It is important to note that, as shown by the *r* values, $\nu_{C=O}$ and $\Delta\nu_{O-H}$ correlate well with all the parameters and that the correlations are better than those shown by the arylideneacetones. A second important result is the demonstration that the sensitivity of the shifts and of the carbonyl frequencies to the electronic influence of a substituent, as shown by the *m* parameters, is also greater for the compounds investigated here. In other words, these compounds have greater electron transmission along their conjugative chains. This is due to the rigidity of the molecules and to the high planarity of the conjugative portion of the cyclohexenone derivatives.

The superior correlations with all parameters also mean that an inductive as well as a conjugative factor is taking part in the electronic interaction in the molecule. For the series of arylideneacetones,[3,4] The Yukawa–Tsuno equation is preferable for two-parameter correlations. For both $\nu_{C=O}$ and $\Delta\nu_{O-H}$, the high sensitivity to inductive influence is observed using this equation. This was surprising because of the distance of attachment of the 3-aryl groups.

In the two sets (a and b) in Table 2, we note that the *m* values are higher in the first, the differences being appreciably greater than the experimental error. This confirms the statement made above about the greater sensitivity of the $\Delta\nu_{O-H}$ values to electronic interaction in the molecule.

Finally, attention is called to an interesting experimental fact. In the i.r. spectra of a majority of the ketones studied in CCl_4 solution, a peak of low intensity or a shoulder on the high-frequency side of the carbonyl band has been detected. This phenomenon may be due to Fermi resonance splitting. The splitting disappears if the medium is changed, for example, from CCl_4 to $CHCl_3$. The same observation has been made previously for other cyclic ketones.[13]

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