# Synthesis and NMR spectral study of some 5-aryl-3-methylcyclohex-2-enones and 5*r*-aryl-3*t*-cyano-3*c*-methylcyclohexanones

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Eight 5-aryl-3-methylcyclohex-2-enones **2a-h** (Ar = $C_6H_5$, *p*-Cl$C_6H_4$, *p*-MeO$C_6H_4$, *p*-$O_2$N$C_6H_4$, *p*-Me$C_6H_4$, *p*-F$C_6H_4$, *p*-$Me_2$N$C_6H_4$ or *m*-$O_2$N$C_6H_4$) and seven 5*r*-aryl-3*t*-cyano-3*c*-methylcyclohexanones **3a-c** and **3e-h** (Ar = $C_6H_5$, *p*-Cl$C_6H_4$, *p*-MeO$C_6H_4$, *p*-Me$C_6H_4$, *p*-F$C_6H_4$, *p*-$Me_2$N$C_6H_4$ or *m*-$O_2$N$C_6H_4$) have been synthesized and characterised by ^{1}H and ^{13}C NMR spectra. For **2a** (Ar = $C_6H_5$) SEFT and HMBC spectra have been recorded. For **2e** (Ar = *p*-Me$C_6H_4$) HSQC and HMBC spectra have been recorded. For **3a** (Ar = $C_6H_5$) HOMOCOSY, NOESY, HSQC and SEFT spectra have been recorded. Analysis of these spectra suggests that cyclohex-2-enones adopt sofa conformation with one of the methylene protons at C-4 and C-6 *anti* to H-5 and the other methylene proton *gauche* to H-5. The effect of the phenyl and methyl groups on the chemical shifts of protons and carbons in cyclohexenone ring are discussed. The cyanocyclohexanones adopt chair conformation with axial orientation of cyano group and equatorial orientations of the methyl and phenyl groups. The probable values for the proton chemical shifts of the various protons in the cyclohexanone ring of *cis*-3-methyl-5-phenylcyclohexanone **6** have been computed from the observed proton chemical shifts of **3a** and the known effects of axial cyano group. The possible values for the ^{13}C chemical shifts of the cyclohexanone ring carbons in **6** have been computed from the ^{13}C chemical shifts of cyclohexanone and known effects of phenyl and methyl groups. Comparison of these values with the chemical shifts of protons and carbons in **2a** suggests that the double bond at C-2 influences the ^{1}H chemical shifts by polarization, magnetic anisotropy and electronegativity effects and the ^{13}C chemical shifts by polarization and electronegativity effects.

**Keywords**: Cyclohex-2-enones, cyanocyclohexanones, ^{1}H NMR, ^{13}C NMR, conformation

Cyclohex-2-enones are useful in the synthesis of organic compounds[1-4]. Attempts to prepare β-cyano-ketones by the addition of hydrocyanic acid to α,β-unsaturated ketones have resulted in the formation of mixture of products[5-7]. However, β-cyanoketones are formed exclusively when α,β-unsaturated ketones are treated with a mixture of $NH_4Cl$ and KCN[8]. Though a number of NMR spectral studies[9-17] have been made on saturated six-membered compounds with and without heteroatoms in the ring, to our knowledge, only one NMR spectral study[18] has been reported on cyclohexenones. Even in this study the chemical shifts and coupling constants for the protons on saturated carbons have not been determined precisely.

There are several NMR spectral studies[10-12,14] on heterocyclic ketones, reporting the ^{1}H chemical shifts and proton-proton coupling constants precisely. However, such studies are rare on cyclohexanones. Recently, for the heavily substituted 2*r*,4*c*-biscarbalkoxy-3*t*-aryl-5*c*-hydroxy-5*t*-methylcyclohexanones **1** such data have been reported[15-17]. However, it is desirable to investigate cyclohexanones with less number of substituents.

This paper reports the synthesis and NMR spectral study of eight 5-aryl-3-methylcyclohex-2-enones **2a-h** and seven 5*r*-aryl-3*t*-cyano-3*c*-methyl-cyclohexanones **3a, 3b, 3c, 3e, 3f, 3g** and **3h**.
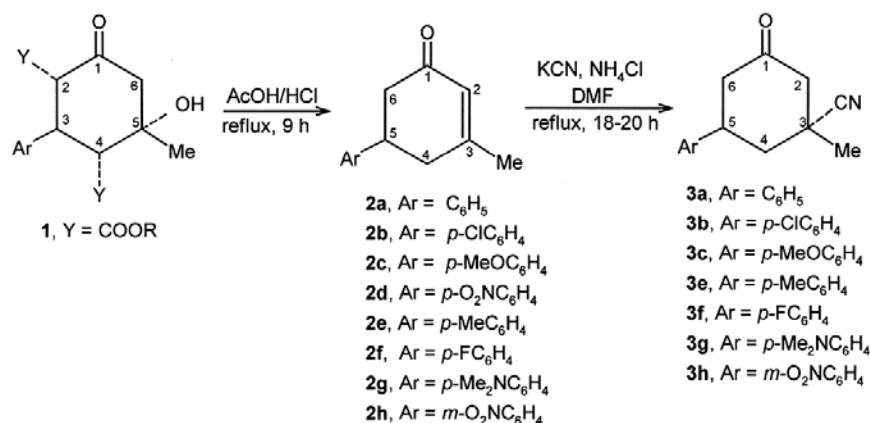
## Results and Discussion

### Synthesis and characterisation of compounds

Compounds included in the present study were obtained from **1** (Ref. 15-17), by reactions shown in **Scheme I**. The numbering of carbon atoms also is shown in **Scheme I**. All compounds were characterised by their IR spectra. Elemental analysis was done for **2b, 2c, 2d** and **3a**. Mass spectrum was recorded for **3a**. The physical data are given in **Table I** and the results of elemental analysis are given in **Table II**.

### Cyclohex-2-enones 2a-h

In the ^{1}H NMR spectrum of **2a** the aromatic protons appeared as a multiplet at δ 7.32. There was a

**Scheme I**

**Table I —** Physical data on cyclohexenones and cyanocyclohexanones

| Ar | 2 | | | 3 | | |
|---|---|---|---|---|---|---|
| | Yield % | m.p. °C | IR cm$^{-1}$ | Yield % | m.p. °C | IR cm$^{-1}$ |
| $C_6H_5$ | 60 | Liquid | 1685 | 85 | 95 | 1715, 2231 |
| $p$-ClC$_6$H$_4$ | 72 | 55 | 1662 | 70 | 85 | 1710, 2235 |
| $p$-MeOC$_6$H$_4$ | 69 | 67 | 1659 | 70 | 61 | 1717, 2235 |
| $p$-O$_2$NC$_6$H$_4$ | 65 | 120 | 1659 | | | |
| $p$-MeC$_6$H$_4$ | 80 | 42 | 1667 | 80 | 103 | 1707, 2235 |
| $p$-FC$_6$H$_4$ | 70 | 45 | 1664 | 65 | Liquid | 1718, 2230 |
| $p$-Me$_2$NC$_6$H$_4$ | 65 | 47 | 1659 | 80 | 115 | 1711, 2235 |
| $m$-O$_2$NC$_6$H$_4$ | 75 | 105 | 1659 | 70 | 114 | 1722, 2238 |

**Table II** — Results of elemental analysis of typical compounds **2b-d** and **3a**

| Compound | Experimental (%) | | | Calculated for the molecular formula (%) | | |
|---|---|---|---|---|---|---|
| | C | H | N | C | H | N |
| **2b** | 70.68 | 5.94 | | 70.75 | 5.90 | |
| **2c** | 77.70 | 7.51 | | 77.78 | 7.41 | |
| **2d** | 67.46 | 5.70 | 6.13 | 67.53 | 5.63 | 6.06 |
| **3a** | 78.89 | 6.99 | 6.82 | 78.87 | 7.04 | 6.57 |

singlet at δ 6.00 due to H-2. The benzylic proton H-5 appeared as a multiplet at δ 3.34. The methylene protons at C-4 and C-6 appeared as a overlap of two AB parts in the range 2.4-2.6 ppm. The methyl protons at C-3 appeared as a singlet at δ 2.03. The $^{13}$C NMR spectra of **2a-h** were almost identical except for the aromatic part.

In the $^{13}$C NMR spectrum of **2a** the carbonyl carbon appeared at δ 199.1. There were two weak signals at δ 161.7 and 143.3, which were assigned to C-3 and *ipso* carbon, respectively. Two strong signals at δ 127.0 and 128.8 were assigned to the *ortho* and

*meta* carbons of the phenyl group. There were two signals at δ 126.8 and 126.6 with almost half the intensity of the signals at δ 127.0 and 128.8. There were three signals at δ 43.9, 40.8 and 39.0 due to the saturated carbons of the cyclohexenone ring. The carbon of the methyl group at C-3 appeared at δ 24.4. From the SEFT spectrum of **2a** it was found that the signals at δ 43.9 and 39.0 are due to methylene carbons. From the HMBC spectrum of **2a** it was found that the signal at δ 39.0 is due to C-4 because this signal had a correlation with the methyl protons. From the other correlations in the HMBC spectrum of **2a** and from the correlations in the HSQC and HMBC spectra of **2e** the signals in the $^1$H and $^{13}$C NMR spectra of cyclohex-2-enones **2a-h** could be assigned unambiguously. The $^1$H and $^{13}$C signals of the aromatic ring in **2b-h** were assigned by known substituent effects[19,20]. In **2b-h** the signals due to C-2 was distinguished from the signals for the other aromatic carbons based on intensity.

From the HSQC spectrum of **2e** it was found that the AB part due to the methylene protons at C-6 is at a higher frequency than that due to the methylene protons at C-4. The first six lines of this AB part

could be clearly seen. From the frequencies of these six lines the coupling constants $J_{5,6}$, $J_{5',6}$ and $J_{5,5'}$ were calculated using second-order analysis. The correct chemical shifts of the methylene protons H-6 and H-6′ were also calculated. The frequencies of all lines in the signal for H-5 were given by the computers in the case of **2a**. The spacing between the first and last lines should correspond to the sum of $J_{5,6}$ $J_{5',6}$, $J_{4,5}$ and $J_{4',5}$. Hence, the sum of $J_{4,5}$ and $J_{4',5}$ could be obtained for **2a**. In all cases the $J_{5,6}$, $J_{5',6}$ and $J_{5,5'}$ could be determined. However, only in the cases of **2a, 2b** and **2f** the sum of $J_{4,5}$ and $J_{4',5}$ could be determined. The proton chemical shifts and coupling constants of **2a-h**

are given in **Table III**. The $^{13}$C chemical shifts are given in **Table IV**.

The chemical shifts of various protons in cyclohex-2-enone **4** (Ref. 21) and 3-methyl-cyclohex-2-enone **5** (Ref. 21) are shown in **Figure 1**. It is seen that in **4** the methylene protons at C-4, C-5 and C-6 give rise to average signals for two interchangeable environments. The appearance of the methylene protons at C-4 and C-6 in **2a-h** as two AB parts suggests that the aryl group at C-5 holds the cyclohex-2-enone ring in a fixed conformation.

Analysis of the *vicinal* coupling constants about the C(5)-C(6) bond, using the method of Slessor and

**Table III** — $^1$H NMR spectral data of cyclohex-2-enones **2a-h**

| Compound | Chemical shifts ($\delta$, ppm)[a] | | | | | | | Coupling constant ($J$, Hz)[b] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | H-2 | H-4 | H-5 | H-6 | H-6′ | CH$_3$ | Aromatic[c] | $J_{5,6}$ | $J_{5,6'}$ | $J_{5,5'}$ |
| **2a** | 6.00 | 2.47 | 3.34 | 2.66 | 2.58 | 2.03 | 7.32 | 4.1 | 13.3 | 16.2 |
| **2b** | 6.03 | 2.55 | 3.36 | 2.67 | 2.57 | 2.07 | 7.38 (*o*) 7.22 (*m*) | 4.1 | 13.5 | 16.1 |
| **2c**[d] | 6.06 | 2.58 | 3.35 | 2.71 | 2.61 | 2.09 | 7.35 (*o*) 6.96 (*m*) | 4.0 | 13.6 | 16.1 |
| **2d** | 6.02 | 2.55 | 3.47 | 2.67 | 2.58 | 2.04 | 7.42 (*o*) 8.23 (*m*) | 4.0 | 13.3 | 16.3 |
| **2e**[e] | 5.99 | 2.54 | 3.30 | 2.64 | 2.56 | 2.03 | 7.20 (*o*) 7.16 (*m*) | 3.9 | 13.7 | 16.4 |
| **2f** | 6.01 | 2.54 | 3.34 | 2.66 | 2.56 | 2.05 | 7.25 (*o*) 7.06 (*m*) | 4.0 | 13.5 | 16.2 |
| **2g**[f] | 6.00 | 2.53 | 3.27 | 2.67 | 2.57 | 2.04 | 7.35 (*o*) 6.77 (*m*) | 3.8 | 13.6 | 16.2 |
| **2h** | 6.00 | 2.54 | 3.44 | 2.67 | 2.56 | 2.02 | 8.12, 7.56 (*o*) 7.51 (*m*) 7.56 (*p*) | 3.5 | 13.6 | 16.1 |

[a] For the methylene protons at C-4 the reported chemical shift corresponds to the centre of the AB part.
[b] The values of ($J_{4,5} + J_{4',5}$) for **2a, 2b** and **2c** were determined as 15.9, 16.1 and 15.1 Hz, respectively.
[c] In the case of aromatic protons *ortho*, *meta* and *para* are with respect to C-5.
[d] The OCH$_3$ protons appeared at 3.89 ppm.
[e] The *p*-Me protons appeared at 2.37 ppm.
[f] The NMe$_2$ protons appeared at 2.89 ppm.

**Table IV** — $^{13}$C NMR spectral data of cyclohex-2-enones **2a-h**

| Compound | Chemical shifts ($\delta$, ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | CH$_3$ at C-3 | Aromatic[a] |
| **2a** | 199.1 | 126.8 | 161.7 | 39.0 | 40.8 | 43.9 | 24.4 | 143.3, 126.6 128.8, 127.0 |
| **2b** | 199.2 | 127.3 | 162.0 | 39.5 | 40.8 | 44.4 | 25.0 | 142.4, 128.8 129.9, 133.3 |
| **2c**[b] | 199.9 | 127.2 | 162.4 | 40.0 | 40.7 | 44.8 | 25.0 | 136.2, 128.3 114.8, 159.2 |
| **2d** | 198.0 | 127.1 | 161.2 | 38.6 | 40.9 | 43.6 | 24.7 | 147.4, 128.1 124.5, 150.9 |
| **2e**[c] | 199.7 | 126.9 | 162.3 | 39.5 | 40.8 | 44.9 | 24.8 | 140.7, 127.0 129.8, 136.9 |
| **2f** | 198.4 | 126.8 | 161.2 | 38.9 | 39.8 | 43.8 | 24.1 | 138.9, 128.1 115.0, 162.7 |
| **2g**[d] | 199.4 | 126.4 | 161.6 | 39.3 | 39.8 | 44.2 | 24.1 | 131.2, 128.2 112.8, 149.5 |
| **2h**[e] | 197.8 | 126.7 | 160.9 | 38.3 | 40.3 | 43.3 | 24.3 | 145.1, 122.1 133.0, 148.5 129.8, 121.7 |

[a] Aromatic signals are mentioned in the order: *ipso*, *ortho*, *meta* and *para*.
[b] OCH$_3$ signal was observed at 56.0 ppm.
[c] *p*-Me signal was observed at 21.5 ppm.
[d] NMe$_2$ signal was observed at 40.5 ppm.
[e] Aromatic carbons are cited in the order *ipso*, *ortho*, *ortho′*, *meta*, *meta′* and *para*.

Tracey[22], suggests that the torsional angle between H-5 and H-6′ is about 175° and that between H-5 and H-6 is about 55°. The observed sum of the *vicinal* coupling constants about C(4)-C(5) bond also suggests that H-5 should be almost *anti* to one of the methylene protons at C-4 and *gauche* to the clear methylene proton at C-4. These torsional angles strongly suggest that compounds **2a-h** adopt sofa conformation shown in **Figure 2**.

Comparison of the chemical shift of H-2 in **2a-h** with that in **5** suggests that the aryl group at C-5 deshields H-2 significantly. This is due to the magnetic field generated by the circulation of $\pi$-electrons in the aryl ring. The aryl group should adopt a conformation so that it is coplanar with C(5)-H(5) bond (**Figure 3**). In such a conformation H-2 should lie in the plane of the aryl group. Though H-2 is at a large distance from the center of the aryl group it should definitely lie in the deshielding region of the aryl group. It is also interesting to note that in **2a-h** H-5 is deshielded by about 1.2 ppm compared to that in **4**.

Comparison of the chemical shift of H-2 in **5** with that in **4** suggests that the 3-methyl group shields H-2 significantly. This is due to the magnetic anisotropic effect of C-CH$_3$ bond[23] (**Figure 4**). A similar shielding should be expected on the methylene protons at C-4. Hence, in **5** the average value of the chemical shifts of the methylene protons at C-4 should be less than that (2.36 ppm) in **4**. It is seen that in **2a-h** the average chemical shift of the methylene protons at C-4 is greater than that in **4**. Thus it is obvious that the aryl group at C-5 deshields the methylene protons at C-4 significantly. It is also obvious that the methylene protons at C-6 are deshielded by the aryl group at C-5.

The $^{13}C$ chemical shifts of cyclohex-2-enone **4** (Ref.. 21) are shown in **Figure 5**. Generally $^{13}C$ chemical shifts are influenced by substituents in $\alpha$ and $\beta$-positions of the particular carbon[24]. A $\gamma$-substituent causes a shielding if it is *gauche* to the concerned carbon. Also a highly electronegative substituent like F, OH or NH$_2$ causes a significant shielding though it is present in the $\gamma$-position *anti* to the concerned carbon[25].

Considering these factors it is obvious that the methyl group at C-3 should influence the chemical shifts of C-2, C-3 and C-4 significantly. Also the aryl group at C-5 should influence the chemical shifts of C-4, C-5 and C-6 significantly. Comparison of the $^{13}C$ chemical shifts of **2a** and **4** suggests that the phenyl group deshields C-5 and C-6 by 18.2 and 5.9 ppm,
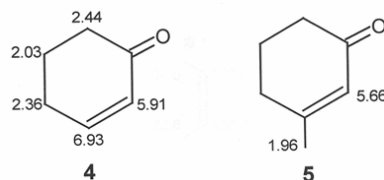


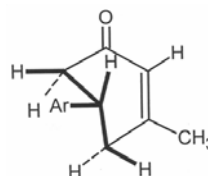Figure 1—Proton chemical shifts of **4** and **5**
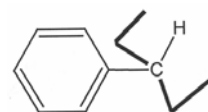


Figure. 2—Conformation of cyclohex-2-enones **2a-2h**


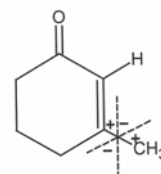
Figure 3—Conformation of phenyl group in **2a**
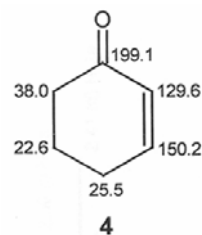


Figure 4—Shielding and deshielding regions of C-CH$_3$ bond



Figure 5—$^{13}C$ chemical shifts of cyclohex-2-eone **4**

respectively. These effects are comparable to the $\alpha$ and $\beta$-effects of phenyl group in *trans*-4-*t*-butylphenyl-cyclohexane[26] which are 17.4 and 7.0 ppm, respectively. In **2a** C-4 is subjected to $\beta$-effect of phenyl and methyl groups. Comparison of the chemical shifts of C-4 in **2a** with that in **4** suggests that the combined $\beta$-effects of phenyl and methyl groups is 13.5 ppm. This is also comparable to the observed value of 12.8 ppm[26] in *t*-butylcyclohexanes. Comparison of chemical shifts of C-2 and C-3 in **3a** with those in **4** suggests that the CH$_3$ group deshields

C-3 ($\alpha$-carbon) by 11.5 ppm and shields C-2 ($\beta$-carbon) by 2.7 ppm.

## Cyanocyclohexanones 3a-c and 3e-h

Reaction of KCN and NH$_4$Cl with cyclic $\alpha,\beta$-unsaturated ketones results in the formation of $\beta$-cyanoketones[8]. The reaction occurs by 1,4-addition followed by the transfer of a proton from oxygen to the $\alpha$-carbon (**Scheme I**). Reaction of **2** with KCN and NH$_4$Cl can give rise to two stereoisomers **3** and **3′**. Since saturated six-membered ring compounds have been shown to exist largely in chair conformation with equatorial orientations of bulky substituents the expected products should adopt conformation **3C** and **3′C**, respectively.

In the $^1$H NMR spectrum of **3a** there was a triplet at δ 7.35 with $J = 7.4$ Hz, corresponding to two protons. This signal should be due to the *meta* protons of the phenyl group. There was a triplet at δ 7.26 with $J = 7.3$ Hz corresponding to one proton. This signal should be due to the *para* proton of the phenyl group. There was a doublet at δ 7.23 with $J = 7.2$ Hz corresponding to two protons. This signal should be due to the *ortho* protons of the phenyl group. In the observed spectrum the third line of the signal due to the *para* proton and the first line of the signal due to the *ortho* protons had overlapped.

There was a triplet of triplet at δ 3.36 corresponding to one proton. This signal should be due to the benzylic proton H-5. The benzylic proton is involved in two diaxial (*trans*) couplings viz., $J_{5a,6a}$ and $J_{4a,5a}$. It is also involved in two small *cis* couplings viz., $J_{5a,6e}$ and $J_{4e,5a}$. Sixteen lines with same intensity should be expected due to these couplings. However, the closely spaced lines overlap resulting in a triplet of triplet (**Figure 6**).

There was a singlet at δ 1.54, corresponding to three protons, due to the methyl protons. There were six one-proton signals in the range 1.9-2.7 ppm. These signals were assigned based on the observed correlations in the HOMOCOSY and NOESY spectra. The spectrum in this region along with the assignments is shown in **Figure 7**. The signal due to H-4a and H-6a appear as triplets instead of the expected double-doublets due to the overlap of the middle two closely spaced lines (**Figure 8**). This is again due to a small difference between $J_{gem}$ and $J_{aa}$ values. However, the spacing between the first and third lines of the observed triplets should give the sum of $J_{gem}$ and $J_{aa}$. The signals for H-4e and H-6e must be
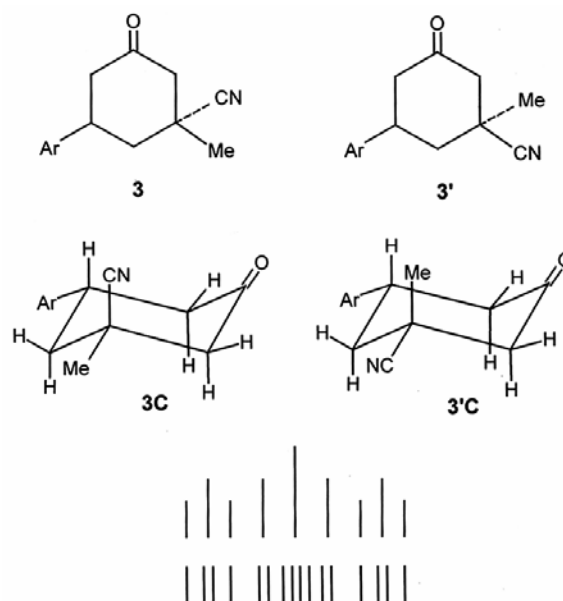


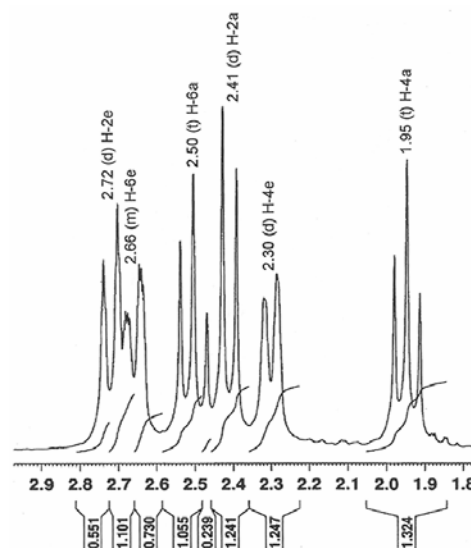**Figure 6**—Overlap of lines for H-5



**Figure 7**—Proton NMR spectrum of **3a**



**Figure 8**—Overlap of lines for H-4a and H-6a

double-doublets. However, in the signal for H-6e additional splittings are seen. The signals for H-2e has four shoulders (each line of the doublet has two

shoulders). Though the signal for H-4e is not well resolved it also has same shoulders. These observations suggest that there is long range coupling among H-2e, H-4e and H-6e. This was also shown by the HOMOCOSY spectrum.

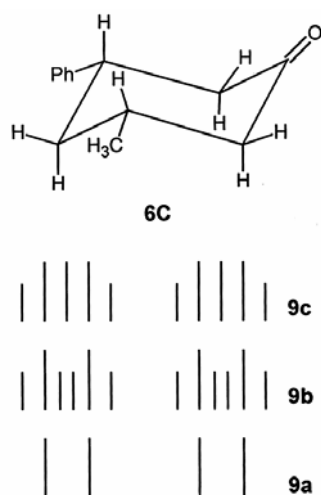In the case of **3e** the signal due to H-6e contained



**Figure 9**—Overlap of lines for H-6e in **3e**

ten lines and that due to H-2e appeared as a triplet of doublet. This observation confirms the long range couplings among the three equatorial protons. The appearance of ten lines for H-6e can be explained as follows. H-6e undergoes coupling with H-6a and H-5a resulting in a doublet of doublet as shown in **Figure 9a**. Due to nearly equal long range couplings with H-4e and H-2e each line is split into a triplet as shown in **Figure 9b**. In the resulting six lines the middle two lines overlap resulting in the observation of 10 lines (**Figure 9c**). Indeed the intensities of lines 1, 5, 6 and 10 were about half of the intensities of the other six lines. Among these 10 lines, spacing between the first and sixth line should correspond to $J_{6a,6e}$. Indeed it was found that the spacings $v_1$-$v_6$, $v_2$-$v_7$, $v_3$-$v_8$, $v_4$-$v_9$ and $v_5$-$v_{10}$ had a constant value of 14.5 Hz. This value is $J_{6a,6e}$. The spacings $v_1$-$v_2$, $v_2$-$v_3$, $v_3$-$v_4$, $v_4$-$v_5$, $v_6$-$v_7$, $v_7$-$v_8$, $v_8$-$v_9$ and $v_9$-$v_{10}$ must correspond to the long range coupling. The average of these values was found as 1.9 Hz. Also the spacings $v_2$-$v_4$ and $v_7$-$v_9$ should correspond to $J_{6a,5a}$. Average of these values was found as 4.2 Hz.

In the case of **3a** six frequencies with almost same

**Table V** — Proton chemical shifts ($\delta$, ppm) of cyanocylohexanones **3a-c** and **3e-h**

| Compound | Chemical shifts ($\delta$, ppm) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | H-2e | H-2a | H-4e | H-4a | H-5a | H-6e | H-6a | CH$_3$ | Aromatic[a] |
| **3a** | 2.72 | 2.41 | 2.30 | 1.95 | 3.36 | 2.66 | 2.50 | 1.54 | 7.23, 7.35, 7.26 |
| **3b** | 2.78 | 2.37 | 2.36 | 1.95 | 3.41 | 2.72 | 2.49 | 1.57 | 7.24, 7.36 |
| **3c**[b] | 2.75 | 2.38 | 2.31 | 1.89 | 3.35 | 2.67 | 2.45 | 1.56 | 7.16, 6.89 |
| **3e**[c] | 2.76 | 2.46 | 2.34 | 1.88 | 3.37 | 2.70 | 2.45 | 1.55 | 7.16, 7.12 |
| **3f** | 2.76 | 2.41 | 2.33 | 1.92 | 3.38 | 2.68 | 2.47 | 1.57 | 7.21, 7.05 |
| **3g**[d] | 2.75 | 2.36 | 2.31 | 1.87 | 3.32 | 2.68 | 2.45 | 1.55 | 7.12, 6.77 |
| **3h** | 2.83 | 2.42 | 2.40 | 2.00 | 3.57 | 2.77 | 2.52 | 1.61 | 8.15, 8.17, 7.57, 7.61 |

[a] Chemical shifts are cited in the order *ortho*, *meta* and *para*.
[b] The OCH$_3$ protons appeared at 3.80 ppm.
[c] The *p*-Me protons appeared at 2.34 ppm.
[d] The NMe$_2$ protons appeared at 2.95 ppm.

**Table VI** — Proton-proton coupling constants (*J*, Hz) in cyanocyclohexanones **3a-c** and **3e-h**

| Compound | Coupling constants (*J*, Hz) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $J_{2a,2e}$ | $J_{4a,4e}$ | $J_{4a,5a}$ | $J_{4e,5a}$ | $J_{5a,6a}$ | $J_{5a,6e}$ | $J_{6a,6e}$ | $J_{ee}$ |
| **3a** | 14.5 | 13.4 | 13.1 | 3.2 | 13.4 | 3.9 | 14.3 | 2.0 |
| **3b** | 14.5 | 13.4 | 13.2 | 3.1 | 13.2 | 4.1 | 14.5 | 2.0 |
| **3c** | 14.5 | 13.5 | 13.0 | 3.1 | 13.3 | 3.9 | 14.4 | 2.0 |
| **3e** | 14.5 | 14.5 | 13.0 | 3.5 | 13.3 | 3.9 | 14.5 | 1.9 |
| **3f** | 14.5 | 13.3 | 13.2 | 3.0 | 13.2 | 4.0 | 14.4 | 2.0 |
| **3g** | 14.5 | 13.7 | 12.8 | 3.1 | 13.3 | 4.0 | 14.4 | 2.0 |
| **3h** | 14.5 | 13.5 | 13.0 | 2.8 | 13.4 | 4.2 | 14.5 | 2.0 |

**Table VII** — $^{13}$C chemical shifts ($\delta$, ppm) of cyanocyclohexanones **3a-c** and **3e-h**

| Compound | Chemical shifts ($\delta$, ppm) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | CH$_3$ | C≡N | Aromatic[a] | Others |
| **3a** | 204.9 | 50.3 | 36.2 | 42.7 | 40.5 | 47.1 | 26.8 | 122.1 | 141.8, 126.3, 128.6, 127.6 | |
| **3b** | 204.3 | 50.6 | 36.3 | 43.1 | 40.1 | 47.3 | 27.3 | 122.1 | 140.5, 127.9, 129.1, 133.0 | |
| **3c** | 205.3 | 50.3 | 36.1 | 43.0 | 39.8 | 47.4 | 26.9 | 122.2 | 134.0, 127.3, 114.0, 158.4 | 55.0 (OCH$_3$) |
| **3e** | 205.0 | 51.0 | 36.6 | 43.8 | 40.6 | 47.8 | 27.7 | 122.0 | 139.4, 126.6, 129.7, 137.3 | 21.2 (CH$_3$) |
| **3f** | 205.1 | 50.6 | 36.5 | 43.2 | 40.2 | 47.6 | 27.2 | 122.5 | 138.1, 128.3, 115.8 (d, J = 21.0 Hz) 161.8 (d, J = 244 Hz) | |
| **3g** | 205.6 | 50.8 | 36.5 | 43.8 | 40.1 | 47.9 | 27.4 | 122.6 | 130.6, 127.3, 113.3, 149.6 | 40.9 N(CH$_3$)$_2$ |
| **3h**[b] | 203.6 | 50.7 | 36.4 | 42.9 | 40.4 | 47.1 | 27.4 | 121.8 | 144.1, 121.3, 138.5, 148.8, 126.8, 122.0 | |

[a]Aromatic signals are cited in the order *ipso, ortho, meta, para.*
[b]Aromatic carbons are cited in the order *ipso, ortho, ortho′, meta, meta′* and *para.*

intensity were given by the computer. Obviously, in this case the lines 1, 5, 6 and 10 with half intensity of the other lines have not appeared clearly. This may be due to the recording of the $^1$H NMR spectrum of **3e** at 500 MHz and that of **3a** at 400 MHz. However, even in this case the values of $J_{5a,6a}$, $J_{6a,6e}$ and long range coupling could be computed from the observed six frequencies.

From the frequencies of the three lines for H-6a the value of $J_{5a,6a}$ could be computed since the value of $J_{6a,6e}$ is known. From the data for H-4e and H-4a the values of $J_{4a,4e}$ and $J_{4a,5a}$ could be computed.

Though $J_{2e,4e}$, $J_{4e,6e}$ and $J_{6e,2e}$ may be expected to be nearly equal the values $J_{5a,6e}$ and $J_{5a,4e}$ may differ significantly. Hence, in the signal for H-5 the spacing between the first and second lines may not correspond to either $J_{5a,4e}$ or $J_{5a,6e}$. However, the spacings $\nu_2$-$\nu_3$, $\nu_5$-$\nu_6$ and $\nu_7$-$\nu_9$ of this signal should give the sum of $J_{5a,4e}$ and $J_{5a,6e}$. From the known value of $J_{5a,6e}$ the value of $J_{5a,4e}$ could be computed. Such calculations could be made for all compounds except **3b**.

The $^{13}$C signals of **3a** could be assigned based on positions, intensities, SEFT spectrum and the correlations in the HSQC spectrum. The $^{13}$C signals for the other cyanocyclohexanones were assigned by comparison with **3a**. In **3b**, **3c** and **3e-3h** the aromatic $^1$H and $^{13}$C signals were assigned based on known substituent effects[19,20]. The various proton chemical shifts of the cyanocyclohexanones are given in **Table V**. The various proton-proton coupling constants are given in **Table VI**. The $^{13}$C chemical shifts are given in **Table VII**.

From the NOESY spectrum of **3a** it was inferred that the methyl protons have strong NOE with H-2a, H-2e, H-6a and H-6e. However, there was no NOE between the methyl protons and H-5. From the observed vicinal coupling constants and NOEs it is obvious that compound **3a** should exist in conformation **3aC** (**3C** with Ar = C$_6$H$_5$). Indeed from the X-ray crystallographic study[27], of **3a** it has been found that **3a** exists in chair conformation **3aC**. Also X-ray crystallographic study[28] of **3h** has shown that it adopts chair conformation **3hC** (**3C** with Ar = *m*-NO$_2$C$_6$H$_4$).

It has been found[29] that an equatorial methyl group shields an adjacent axial proton by 0.42 to 0.45 ppm, whereas an axial methyl group deshields it by 0.16-0.26 ppm. The effect of axial and equatorial cyano groups on the chemical shifts of various protons in cyclohexane have been determined by Abraham and Reid[30]. Based on the effects of the methyl and cyano groups H-2a and H-4a in **3′C** should be deshielded by 0.59-0.72 ppm than those in **3C**. However, in **3b, 3c, 3e, 3f** and **3g** the chemical shifts of H-2a and H-4a differ from those in **3a** only by 0.00-0.08 ppm. Hence, it is obvious that all these compounds should adopt conformation **3C.**

It is of interest to find the effect of the double bond at C-2 on the chemical shifts of the saturated carbons C-4, C-5 and C-6 and the protons on these carbons. This can be done by comparing the chemical shifts of appropriate carbons and protons in 3*r*-methyl-5*c*-phenylcyclohexanone **6** with the corresponding carbons and protons in **2a**. Compound **6** should adopt conformation **6C** with equatorial orientations of the phenyl and methyl groups.

Effect of axial cyano group on all protons in **3a** are available[30] except for H-6e. However, the axial cyano group at C-3 can influence the chemical shifts of protons at C-6 only by magnetic anisotropic effect which depends on the relative orientations of the cyano group and the particular proton. The effect of axial cyano group at C-3 on H-6e may be taken as that of an equatorial cyano group at C-3 on H-6a, for which the value is available. Using the SCS values for cyano group and from the chemical shifts of **3a** the probable values for the chemical shifts of H-4e, H-4a, H-5a, H-6e and H-6a in **6** were computed as 2.01, 1.62, 2.90, 2.58 and 2.45 ppm, respectively. Comparison of these values with those of the corresponding protons (H-4, H-4′), H-5, H-6 and H-6′ in **2a** suggests that the double bond at C-2 deshields all these protons significantly.

From the known effects of phenyl and methyl group[24] on ^{13}C chemical shifts and the chemical shifts of carbon of cyclohexanone[31] the probable chemical shifts of C-4, C-5 and C-6 in **6** were computed as 40.0, 44.0 and 48.9 ppm, respectively. In these calculations the small $\gamma$-anti effects of phenyl and methyl groups were ignored. Comparison of these values with those in **2a** suggests that these carbons are shielded by the double bond at C-2.

It is seen that H-5 is deshielded by 0.44 ppm and C-5 is shielded by 3.2 ppm by the double bond at C-2. This may be due to a polarization of C(5)-H(5) bond by the $\pi$-electron cloud so that H-5 gets a slight positive charge and C-5 gets a slight negative charge. Similar effects by an axial hydroxy group and ^{1}H and ^{13}C chemical shifts have been found as 0.49[29] and 6.7 ppm[24], respectively. Thus, the observed deshielding on H-5 is not proportional to the observed shielding on C-5. Probably, the deshielding on H-5 may be partly due to magnetic anisotropy of the C=C bond.

Also H-6 and H-6′ are shielded by 0.08 and 0.13 ppm, respectively whereas C-6 is shielded by 5 ppm by the double bond at C-2. These effects may be due to a combination of polarization of C-(H-6′) bond, magnetic anisotropic effect and a decrease in the electronegativity of the carbonyl group. The contribution of structure **C** to the resonance should decrease the positive charge on the carbonyl carbon which in turn should decrease the electronegativity of the carbonyl group.

It is seen that H-4 (equatorial like proton) and H-4′ (axial like proton) are deshielded by 0.46 and 0.75 ppm, respectively, by the double bond at C-2. However, C-4 is shielded only by 1.0 ppm by the double bond at C-2. This is in contrast to the observations made on H-6, H-6′ and C-6.

In the cyclohexanone **6** C-3 is a saturated carbon whereas in **2b** it is an olefinic carbon. Furthermore, due to contribution of structure **C** to the resonance the electronegativity of C-3 in enhanced significantly. This increase in electronegativity should deshield H-4, H-4′ and C-4. The polarisation of C-(H-4′) bond shields C-4 but deshields H-4′. Thus, the two effects act in opposite directions for C-4 but in the same direction for H-4′. Hence, H-4′ is deshielded significantly but there is a small net shielding on C-4.

**Experimental Section**
**Preparation of compounds**
**3t-Aryl-2r,4c-dicarbalkoxy-5c-hydroxy-5t-methyl-cyclohexanones 1**

These compounds were prepared following the methods already reported[15-17]. All compounds were purified by recrystallization from ethanol. The melting points were determined and there was good agreement with these reported already. Compounds **2e** and **3e** were prepared starting from 3t-(p-tolyl)-2r,4c-bis(isopropoxycarbonyl)-5c-hydroxy-5t-methylcyclo-hexanone for which the physical and spectral data have not been reported earlier. These are as follows: Yield 80%; m.p. 164 °C. IR: 3483 (for OH); 1735, 1709 cm^{−1} (for C=O). ^{1}H NMR (500 MHz, CDCl₃): $\delta$ 0.61, 1.01, 1.05, 1.10 (doublets each corresponding to 3H, $CH_3$ of $COOCH(CH_3)_2$ at C-2 and C-4); 1.32 (s, 3H, $CH_3$ at C-5); 2.28 (s, 3H, $CH_3$ at phenyl); 2.46 (dd, 1H, $J$ = 3.00, 14.5 Hz, H-6a); 2.68 (d, 1H, $J$ = 14.5 Hz, H-6e); 2.96 (d, 1H, $J$ = 12.0 Hz, H-4a); 3.58 (d, 1H, $J$ = 12.5 Hz, H-2a); 3.75 (d, $J$ = 2.5 Hz, OH at C-5); 3.93 (t, 1H, $J$ = 12.3 Hz, H-3a); 4.77, 4.80 (multiplets each corresponding to 1H, CH of $COOCH(CH_3)_2$ at C-2 and C-4); 7.26, 7.09 (aromatic protons). ^{13}C NMR (125 MHz, CDCl₃): 20.9, 21.7 ($CH_3$ of $COOCH(CH_3)_2$ at C-2 and C-4); 21.7 ($CH_3$ of p-tolyl); 28.8 ($CH_3$ at C-5); 45.1 (C-3); 53.0 (C-6); 57.4 (C-4); 63.0 (C-2); 68.7, 68.9 (CH of $COOCH(CH_3)_2$ at C-2 and C-4); 73.2 (C-5); 128.3, 129.3 (aromatic carbons); 135.3, 137.5 (*ipso* carbons); 167.4, 173.6 (CO of $COOCH(CH_3)_2$ at C-2 and C-4); 201.5 (C=O).

**5-Aryl-3-methylcyclohex-2-enones 2a-h**

A mixture of the appropriate ketone **1** (0.01 mole) in glacial acetic acid (25 mL) and concentrated

hydrochloric acid (50 mL) was refluxed for 9 hr. After completion of the reaction, the reaction- mixture was neutralized with ammonia and the product was purified by column chromatography using silica gel (100–200 mesh) with benzene-ethyl acetate (9.5:0.5) as eluent.

## 5*r*-Aryl-3*t*-cyano-3*c*-methylcyclohexanones (3a-c and 3e-h)

A mixture of 5-aryl-3-methylcyclohex-2-enones (0.02 mole), potassium cyanide (0.04 mole), ammonium chloride (0.03 mole), dimethylformamide (50 mL) and water (2 mL) was heated and stirred for about 18-20 hr at 80°C. During this time ammonia gas was evolved. The reaction mixture was poured into water and extracted with $CH_2Cl_2$ (30 mL). The organic layer was washed with water and dried over anhydrous sodium sulphate. Evaporation of solvent gave the crude product which was purified by column chromatography using silica gel (100–200 mesh) as adsorbent and hexane-ethyl acetate (4.5:1) as eluent.

## Recording of spectra

### $^1$H NMR spectra

For **2a**, **2d** and **2e** $^1$H NMR spectra were recorded on a Bruker AV 300 NMR spectrometer operating at 300.12 MHz for $^1$H with the following parameters: number of scans 32; data points 32 K; sweep width 6172.84 Hz; acquisition time 2.65 sec. For **2b**, **2c** and **2h** $^1$H NMR spectra were recorded on a Jeol GSX 400 NMR spectrometer operating at 399.65 MHz for $^1$H with the following parameters: number of scans 64; data points 32 K; sweep width 5000 Hz; acquisition time 2.05 sec. The $^1$H NMR spectrum of **3e** was recorded on a Bruker DRX 500 NMR spectrometer operating at 500.03 MHz for $^1$H with the following parameters: number of scans 284; data points 32 K; sweep width 34013.61 Hz; acquisition time 0.48 sec. For all the other compounds $^1$H NMR spectra were recorded on a Bruker AMX 400 NMR spectrometer operating at 400.14 MHz for $^1$H with the following parameters: number of scans 64; data points 16 K; sweep width 7246.38 Hz; acquisition time 1.26 sec. For recording $^1$H NMR spectra, solutions were prepared by dissolving 10 mg of the material in 0.5 mL of $CDCl_3$.

### $^{13}$C NMR spectra

For **2d**, **2e** and **2h** $^{13}$C NMR spectra were recorded on a AV 300 NMR spectrometer operating at 75.48 MHz for $^{13}$C and with the following parameters: number of scans 400; data points 64 K; sweep width 17985.61 Hz; acquisition time 1.82 sec. For **2b**, **2c** and **3e** $^{13}$C NMR spectra were recorded on a Bruker DRX 500 NMR spectrometer operating at 125.77 MHz for $^{13}$C with the following parameters: number of scans 284; data points 16 K; sweep width 31446.54 Hz; acquisition time 0.26 sec. For other compounds $^{13}$C NMR spectra were recorded on a Bruker AMX 400 NMR spectrometer operating at 100.63 MHz for $^{13}$C with the following parameters: number of scans 256; data points 16 K; sweep width 31446. 54 Hz; acquisition time 0.26 sec. For recording $^{13}$C NMR spectra, solutions were prepared by dissolving 50 mg of the material in 0.5 mL of $CDCl_3$.

## 2D NMR spectra

For **3a**, HOMOCOSY, HMBC, HSQC spectra were recorded on a Bruker DRX 500 NMR spectrometer and for **2e**, HMBC and HSQC spectra were recorded on a Bruker AV 300 NMR spectrometer using standard parameters. Phase sensitive NOESY spectrum of **3a** was recorded with a mixing time 1 sec.

For recording 2D NMR spectra, solutions were made by dissolving 50 mg of the material in 0.5 mL of the solvent. The number of data points was 1 K. All NMR measurements were made using 5 mm tubes.

IR spectra recorded on Avatar 330 FT-IR Thermo Nicolet spectrometer in KBr pellets. The mass spectrum of **3a** was recorded on a Jeol DX-303 mass spectrometer. Elemental analyses were performed on a Perkin-Elmer CHNS/O analyser.

## Conclusion

The observed *vicinal* coupling constants of **2a-h** suggest that these compounds adopt a sofa conformation in which C-1, C-2, C-3, C-4, C-6 lie almost in one plane and C-5 lies above this plane. The NMR spectral data of the cyanocyclohexanones suggest that these compounds exist in chair conformation with cyano group in the axial position and the aryl and methyl groups in the equatorial positions. Comparison of chemical shifts of **2a** with the probable value of 3*r*-methyl-5*c*-phenylcyclo-hexenone suggests that the double bond at C-2 influences the chemical shifts of C-4, C-5, C-6 and the protons on these carbons by polarisation, magnetic anisotropy and electronegativity effects.

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