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# A CORRELATION BETWEEN THE CONFIGURATION AND INFRARED BAND INTENSITY OF THE CYANO GROUP IN THE FUSED CYCLOHEXANE RING SYSTEMS *1

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IN the course of our study on the hydrocyanation (1) of polycyclic α,β-unsaturated ketones, we found that configurations of the introduced epimeric cyano groups are closely correlated with the band intensities of the C≡N stretching vibration in the infrared spectra. The present communication treats this correlation.

The molecular extinction coefficient, ε, (2) and the wave number, ν, of a C≡N stretching vibration were carefully measured using a LiF prism in more than 30 pairs of epimeric polycyclic nitriles placed in a rigid conformation except for a few compounds. In every example, it was clearly observed that an equatorial cyano compound shows a higher C≡N band intensity than an axial epimer, despite little fluctuation of the absorption maximum in both epimers. This relation can be easily seen from the values of the intensity ratio, $\epsilon_{eq.}/\epsilon_{ax.}$, in the last column in the table, where data of the representative pairs of epimeric nitriles are collected for more detailed discussion. As to configurations of the cyano groups of angularly cyanated compounds (I - VIII), which were mainly examined because of ready accessibility in this laboratory, it is

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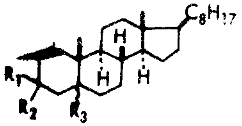
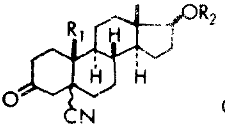
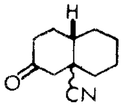
[*1] Angularly Substituted Polycyclic Compounds, XIII.

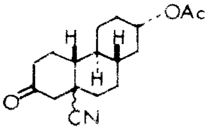
Table. C≡N Stretching Infrared Absorption Data for Typical Polycyclic Cyano Compounds in Chloroform Solution

| | Compound | max. cm$^{-1}$ eq. (cis)$^{b}$ | max. cm$^{-1}$ ax. (trans)$^{b}$ | $\epsilon$ $[C_{\beta}-C_{\gamma}]^{a}$ eq. (cis)$^{b}$ | $\epsilon$ $[C_{\beta}-C_{\gamma}]^{a}$ ax. (trans)$^{b}$ | $\epsilon_{eq.}/\epsilon_{ax.}$ |
|---|---|---|---|---|---|---|
| I | 5-cyanocholestane | 2230 | 2228 | 55.9<br>[2] | 38.9<br>[1] | 1.44 |
| II | 5-cyano-3,3-ethylenedioxycholestane | 2235 | 2234 | 47.3<br>[2] | 32.9<br>[1] | 1.44 |
| III | 5-cyanocholestan-3-ol$^{c}$ | 2232 | 2230 | 43.3<br>[2] | 29.5<br>[1] | 1.47 |
| IV | 5-cyanocholestan-3-one | 2236 | 2235 | 35.2<br>[2] | 26.1<br>[1] | 1.35 |
| V | 5-cyano-17β-propionyloxyandrostan-3-one | 2236 | 2234 | 32.8<br>[2] | 23.8<br>[1] | 1.38 |
| VI | 9-cyano-2-decalone | 2238 | 2236 | 32.9$^{d}$<br>[2] | 18.6<br>[0] | 1.77 |
| VII | 10a-cyano-7α-acetoxy-4aβ,4bα,8aβ-perhydrophenanthren-2-one | 2237 | 2238 | 32.9<br>[2] | 19.0<br>[0] | 1.74 |
| VIII | 5-cyano-17β-acetoxyestran-3-one | 2238 | 2237 | 35.9<br>[2] | 19.9<br>[0] | 1.80 |
| IX | 3-cyano-5α-cholestane | 2242 | 2240 | 65.5<br>[2] | 45.6<br>[0] | 1.44 |









I $R_1 = R_2 = H$, $R_3 = CN$ V $R_1 = CH_3$, $R_2 = COC_2H_5$ VI VII

II $R_1 = R_2 =$  , $R_3 = CN$ VIII $R_1 = H$, $R_2 = COCH_3$

III $R_1 = H$, $R_2 = OH$,$^{c}$ $R_3 = CN$

IV $R_1, R_2 = O$, $R_3 = CN$

IX $R_1, R_2 = <^{H}_{CN}$ , $R_3 = \alpha$-H

[a] The number of parallel $C_{\beta}-C_{\gamma}$ bond with respect to the cyano group. [b] Valid only for angular cyano compounds. [c] The hydroxy group is axially oriented. [d] Despite of the non-rigid ring system, the cis-VI exhibits an $\epsilon$ value not deviating from those of the cis-compounds (cis-V, -VII and -VIII) with rigid structure.

clear that the cyano group in the A/B *cis* nitrile is equatorial to the B-ring whereas the group in the *trans* epimer is axial, as illustrated in Fig. 1. The values of the intensity ratios for the pairs of 5-cyano steroids (examples I-V), irrespective of the species of the substituents at $C_3$, fall into a narrow range of 1.35-1.47, although the $\epsilon$ values themselves are remarkably reduced for the $C_3$-oxygenated steroidal compounds probably due to the negative inductive effect of the substituents. Furthermore, the intensity-configuration relation also holds for the pairs of the bi- and tricyclic cyano compounds (examples VI and VII), as well as for the pair of the non-angular cyano compound (example IX), as clearly shown in the table. It must be noted that, in the angular cyano compounds with rigid conformation , higher values of the intensity ratio, ranging from 1.74-1.80, are observed for the 19-norsteroid type compounds (examples VI, VII and VIII) as compared with the values of 1.35-1.47 for the steroids (examples I-V).

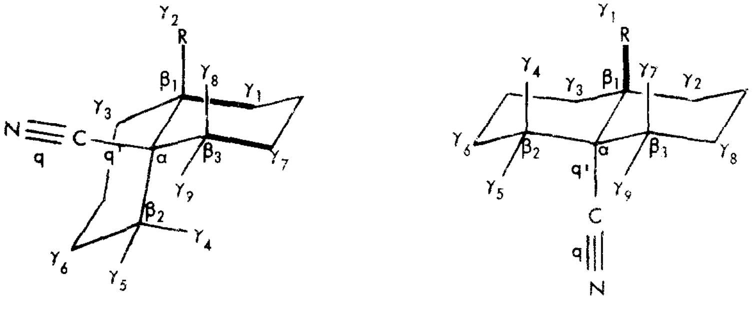
After unsuccessful attempts to explain the configuration-intensity relation, we reached a rather new theoretical interpretation (3). It has been demonstrated (4) that the integrated intensity of a fundamental infrared band is proportional to the expression

$$I_i = \left(\frac{\partial \mu x}{\partial Q_i}\right)^2 + \left(\frac{\partial \mu y}{\partial Q_i}\right)^2 + \left(\frac{\partial \mu z}{\partial Q_i}\right)^2 = \left[\sum_k \frac{\partial \mu x}{\partial R_k} L_{ki}\right]^2 + \left[\sum_k \frac{\partial \mu y}{\partial R_k} L_{ki}\right]^2 + \left[\sum_k \frac{\partial \mu z}{\partial R_k} L_{ki}\right]^2 \quad \cdots\cdots \text{(i)}$$

in which $\mu_x$, $\mu_y$ and $\mu_z$ are components of the dipole moment along an appropriate internal Cartesian coordinate, and $Q_i$ is the normal coordinate corresponding to the fundamental mode under discussion which is related to the internal coordinate $R_k$ by the formula, $R_k = \sum_i L_{ki} Q_i$ . The normal coordinate treatment for $CCl_3CN$ (5) and $CH_3CN$ (6) showed that the vibrational coordinates of C≡N stretching vibration largely consist of the C≡N bond axis q and its adjacent C-C bond axis q'. This statement means that vibrational modes of the C≡N stretching band in the present series of compounds are localized on the C≡N and its adjacent C-C bonds and that the values of $(\frac{\partial\mu}{\partial R_k}L_{ki})$ associated with the C≡N stretching band are of no importance except for those of $(\frac{\partial\mu}{\partial q}L_{qi})$ and $(\frac{\partial\mu}{\partial q'}L_{q'i})$. When the C–C≡N bond axis is taken as the x axis, the x components, $(\frac{\partial\mu_x}{\partial q}L_{qi})$ and/or $(\frac{\partial\mu_x}{\partial q'}L_{q'i})$, are of the largest value and the smaller y and z components almost cancel each other to become negligible as compared with the x components. Then the $I_i$ for equatorial epimer reads as follows,

$$I_i = I_{eq.} = [\frac{\partial}{\partial q}(\mu_{CN} + \mu_{C\alpha} + 3\cdot\frac{1}{3}\mu_{\alpha\beta})L_{qi} + \frac{\partial}{\partial q'}(\mu_{CN} + \mu_{C\alpha} + 3\cdot\frac{1}{3}\mu_{\alpha\beta})L_{q'i} + \frac{\partial}{\partial q'}\{(\mu_{\beta_1\gamma_1} + \mu_{\beta_2\gamma_4} + \mu_{\beta_3\gamma_7}) - \frac{1}{3}(\mu_{\beta_1\gamma_2} + \mu_{\beta_1\gamma_3} + \mu_{\beta_2\gamma_5} + \mu_{\beta_2\gamma_6} + \mu_{\beta_3\gamma_8} + \mu_{\beta_3\gamma_9})\}L_{q'i}]^2 \quad \text{(ii)}$$

where the suffixes of $\mu$ represent the notation of atoms in Fig. 1. It has been reported that the C≡N band intensity increases on passing from methyl cyanide to ethyl and n-propyl cyanide to arrive at a maximum value independent of the chain length (7). This indicates that the contributions from the $C_\beta - C_\gamma$ bonds are not negligible.



cis (eq.) trans (ax.)

steroids : R = $CH_3$

19-norsteroid type compounds : R = H

Fig. 1

We can derive a similar formula $I_{ax.}$ for the axial epimer in the same way. Considering the similarity in the molecular structure and the equality in the C≡N band frequency between axial and equatorial epimers, the values of $L_q$ and $L_{q'}$ in the formula for $I_{eq.}$ may be set equal to those for $I_{ax.}$ respectively. Therefore, $\frac{\partial}{\partial q}(\mu_{CN} + \cdots)L_{qi} + \frac{\partial}{\partial q'}(\mu_{CN} + \cdots)L_{q'i}$ in equation (ii) can be replaced by the common K for both $I_{eq.}$ and $I_{ax.}$ Postulating that the values of the nine derivatives, $\frac{\partial \mu_{\beta\gamma}}{\partial q'}$, in the last parenthesis which probably originate in the inductive effect are independent of the orientation of the β-γ bonds with respect to the C–C≡N bond, we can simplify the equation by replacing the $\mu_{\beta\gamma}$ value with C-H bond moment, $\mu_{CH}$, or C-C bond moment, $\mu_{CC}$. Then, the intensity ratio, $I_{eq.}/I_{ax.}$, is given by

$$\frac{I_{eq.}}{I_{ax.}} = \frac{[K + \{\frac{\partial}{\partial q'}(\mu_{CC} - \frac{1}{3}\mu_{CH})\} L_{q'i}]^2}{[K + \{\frac{\partial}{\partial q'}(\mu_{CH} - \frac{1}{3}\mu_{CC})\} L_{q'i}]^2} = 1 + \frac{8}{3}\frac{\partial}{\partial q'}(\mu_{CC} - \mu_{CH})L_{q'i}/K \quad \cdots\cdots\cdots \text{(iii)}$$

The value of $\frac{\partial}{\partial q'}(\mu_{CC} - \mu_{CH})L_{q'i}/K$ can be estimated to be of sufficient magnitude for the observed ratio on the basis of the inductive effect expressed by $h_{C_n} = (\frac{1}{3})^n h_x$ in the MO method (8), as will be discussed in a full paper. For 19-norsteroid type compounds we get

$$I_{eq.}/I_{ax.} = 1 + (16/3)\{\frac{\partial}{\partial q'}(\mu_{CC} - \mu_{CH})L_{q'i}/K\} \quad \cdots\cdots\cdots\cdots\cdots \text{(iv)}$$

A comparison of the equation (iii) with (iv) affords an excellent explanation for the observation that the relative increments in intensity, $(\epsilon_{eq.}/\epsilon_{ax.})-1$, for the 19-norsteroid type compounds are twice those for the steroids, as noted earlier.

This theoretical treatment further leads to the conclusion that so far as the structural environments surrounding the C–C≡N bond are almost equal, the increase in C≡N band intensities are governed mainly by the number of the $C_\beta$-$C_\gamma$ bonds parallel to the C≡N bond (bold line in Fig. 1). This is clearly demonstrated by comparison of the observed values of the angular cyano keto compounds (IV, V, VI, VII and VIII). Thus, as can be seen from Fig. 1 and the table, the trans-19-norsteroid type compounds (trans-VI, -VII and -VIII) possessing no parallel $C_\beta$-$C_\gamma$ bond show the lowest ε value of $\epsilon$ 18.6-19.9, the trans-steroids (trans-IV and -V) possessing one such a bond show the middle values of 23.8-26.1 and finally the cis-compounds of both 19-norsteroid type compounds and steroids (cis-VI, -VII, -VIII, -IV and -V) possessing inherently two such bonds show the highest $\epsilon$ values of 32.8-35.9.

We believe that this both empirically and theoretically established correlation between the configuration and the C≡N band intensity is widely applicable for configurational assignment of the cyano group attached to a cyclohexane ring system, at least when the molecules of the cyano compounds are placed in a rigid conformation and the two stereoisomers are available. Further extension of this correlation to the cyano compounds with a non frozen conformation or to other functional groups than a cyano group is the next purpose of our investigation.

## References

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2. Here $\epsilon$ was used instead of the integrated intensity because the half band width was almost constant throughout the compounds examined and was of the same value within the epimers.
3. The theoretical treatment was carried out mainly by H. W.
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