Interactions Between Cyano-group and Sulphur Atom in Some α- and β-Ethylthio-nitriles

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Summary Some α-ethylthio-nitriles show a different kind of interaction between the sulphur and cyano group than the corresponding β-compounds as indicated by i.r., n.m.r. and u.v. measurements.

OUR recent studies have shown[1-3] that the replacement of α-hydrogen by the ethylthio-group in some carbonyl compounds leads to a slight decrease of basicities and that this is accompanied by a decrease of carbonyl frequencies. It was suggested that this abnormal relationship could be due to some transfer of charge density from the carbonyl group to a vacant orbital on the sulphur atom, although the possibility of steric hindrance to hydrogen bonding has not been excluded.

We now report some experimental results indicating that α-ethylthio-nitriles in which steric complications are absent, also show a decrease of both basicity and cyano-group stretching frequency, in comparison with the corresponding unsubstituted compounds. Consequently, it seems reasonable to suggest that transfer of charge density from the cyano-group to a vacant orbital on the sulphur atom occurs.

The relative basicities were determined by two methods: n.m.r. measurement of CH shifts for phenylacetylene–nitrile systems and the extent of the unusual increase of the C⋮N stretching frequencies in the presence of high concentrations of phenol. The latter is known to follow the hydrogen bonding ability of the lone pair of electrons on the nitrogen atom.[4] The results are shown in the Table.

Stretching vibrations of CN, *the shifts of* CN *band in the presence of phenol, and n.m.r. data for hydrogen bonding between phenylacetylene and some nitriles*

	Compound RCN R	ν(CN)[a] (cm⁻¹)	Δν(CN)[b] (cm⁻¹)	Δν(⋮CH)[c] (Hz)
(1)	Et	2251	9·7	31·7
(2)	Bu^n	2255	8·9	30·0
(3)	Pr^i	2247	9·5	31·0
(4)	$EtS{\cdot}CH(CH_3)$	2244	6·5	23·8
(5)	$EtS{\cdot}C(CH_3)_2$	2236	8·1	28·1
(6)	$EtS{\cdot}[CH_2]_2$	2255 2249^{sh}	10·7	36·8

[a] In CCl_4. [b] See ref. 4 for details of conditions. [c] See ref. 3 for details of conditions.

The plot of the values of Δν(CN) against Δν(⋮CH) (Figure) gave a linear correlationship. The correlation coefficient was calculated to be 0·973. Thus, it can be concluded that two different methods give the same basicity relationship. In fact, the Table and the Figure illustrate that the α-ethylthiopropionitrile (4) and α-ethylthioisobutyronitrile (5) show a decrease of the basicity and a shift of the cyano-group stretching to lower frequencies in comparison with the unsubstituted compounds (1—3). The Table and the Figure show also that, unexpectedly, the β-ethylthionitrile (6) exhibits an increase of basicity in comparison with the unsubstituted nitriles. Although the i.r. spectrum of this compound shows a C⋮N stretching band of normal frequency it is accompanied by a shoulder at slightly lower frequency which is absent in the unsubstituted compounds.

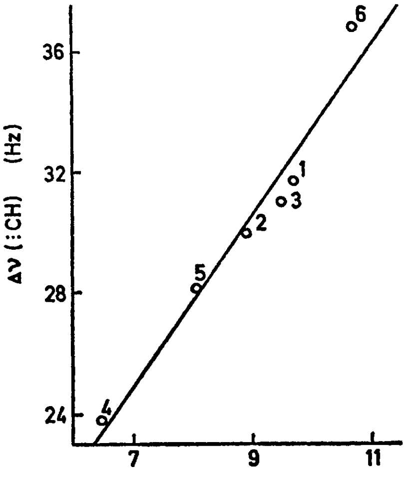

FIGURE. *Plot of* Δν *for phenylacetylene–nitrile systems by n.m.r. spectroscopy against* Δν *values for* CN *bonded to phenol. The key to the numbering of the points is in the Table.*

It seems reasonable to suggest that the interaction in the β-ethylthio-nitrile (6) may be of a charge-transfer type due to the donating ability of the sulphur atom, similar to the transannular interaction reported for the β-thiacyclanones[5,6] and some mesocyclic thiaketones.[7,8] We are not aware of any recorded case of this type of interaction occurring in the acyclic β-alkylthio-carbonyl compounds.

Finally, the u.v. spectra of the α-ethylthiopropionitrile (4) and α-ethylthioisobutyronitrile (5) exhibit a broad band in n-hexane at 237 nm (log ε 2·2—2·9) of similar wavelength and intensity to those in the α-alkylthioketones[9] (240—248 nm; log ε 2·6) and in some α-thiacyclanones[6] (250 nm; log ε 2·4—2·6). This is, probably, due to the excited-state charge-transfer in the interacting $-S-CH_2-CN$ system.

We thank the Ford Foundation and the "Fundação de Amparo à Pesquisa do Estado de São Paulo" for support, and the Organization of American States for a scholarship. (to C. C. S.)

(*Received, 22nd October* 1971; *Com.* 1858.)

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