Hyperconjugation in Dicyano Methane and 2,2-Dicyano Propane

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Photoelectron spectra, hyperconjugation, methylene derivatives

The photoelectron (PE) spectra of dicyano methane and of its dimethyl derivative are tentatively assigned on the basis of a simple MO model. The interactions defined therein between the two cyano groups as well as with the \text{R}_2\text{C}-framework can be parametrized using the PE data. Thus the hyperconjugation $\pi_{\text{CN}}/\pi_{\text{CR}}$ is estimated to amount to 1.7 eV in both compounds. Hyperconjugative effects in methane derivatives $\text{H}_2\text{CX}$ and $\text{H}_2\text{CX}_2$ with $X = \text{Br}$, Cl and CN are compared.

Additional “through bond” interactions with $\sigma$ orbitals of the same irreducible representations destabilize all orbitals except $1_a$, which therefore might serve as an internal standard in dicyano methane.

The applicability of this simple model to compounds $\text{R}_2\text{C(CN)}_2$ will be tested in the following by its PE spectroscopic parametrization.

A. Dicyano Methane

Orbital construction

Dicyano methane contains 24 valence electrons occupying 12 molecular orbitals. These can be constructed starting from the following linear combinations of bond orbitals (LCBO) characterized by their symmetry species (3).

\[
\begin{array}{c|cccc}
\text{MO} & b_2 & a_2 & b_1 & a_1 & \Sigma \\
\hline
\pi_{\text{CN}} & 1 & 1 & 1 & 1 & 4 \\
\pi_{\text{CN}} & 1 & - & - & 1 & 2 \\
\sigma_{\text{CN}} & - & 1 & 1 & 2 & 5 \\
\sigma_{\text{CN}} & 2 & - & - & 4 & 12 \\
\Sigma & 4 & 1 & 2 & 5 & 12 \\
\end{array}
\]

Mixing of all symmetry equivalent basis orbitals according to their overlap and energy differences yields molecular orbitals, which may be classified as $\pi$, $\sigma$ and $n_{\text{N}}$. 
The systems in and perpendicular to the molecular plane are formed mainly from the orbitals \( \pi_{\text{CN}} \) and \( \sigma_{\text{CH}} \). The symmetry controlled \( \pi/\sigma \) interactions are sketched out in the simplified MO diagram (2), in which the lower lying orbitals \( 2a_1 \) and \( 1a_1 \) — although not shown — were taken into account, destabilizing \( 3a_1 \). On the other hand the \( \pi/\sigma \) interactions between the \( b_2 \) orbitals can be neglected approximatively because of the large energy gap. Missing numbering of \( \pi(a_1) \) and \( \pi(b_2) \) is due to the yet undetermined position of the nitrogen lone pairs \( n_N \). Obviously, the \( \pi \) orbital \( b_2 \) lies above \( a_2 \), and \( b_1 \) probably\(^8\) above \( a_1 \). Other sequences remain uncertain. Assuming validity of Koopmans theorem\(^4\) the MO model (2) helps in assigning the PE spectrum.

The nitrogen lone pairs \( n_N \), although expected in the region of the \( \pi_{\text{CN}} \) orbitals are almost orthogonal to them and therefore may be treated separately. Their symmetry adapted combinations \( n_N^-(b_2) \) and \( n_N^+(a_1) \) should remain energetically degenerate as far as through space interaction is considered, because the two nitrogen atoms are separated by about 4 Å\(^8\).

According to the \( n/n \) interaction model by Hoffmann, Imamura, and Hehre\(^6\) both the \( n_N^-(b_2) \) and \( n_N^+(a_1) \) combinations should be destabilized by through bond interactions to approximately the same extent, because of the even number of intervening \( \sigma \) bonds. This implies, that there are equal numbers of \( \sigma \) \( (a_1) \) and \( \sigma \) \( (b_2) \) orbitals at comparable energetic distances, and that the influence of the \( \sigma_{\text{CH}}(3a_1) \) in excess is roughly compensated by the corresponding unoccupied \( \sigma_{\text{CH}}^+(a_1) \). On the contrary, the generally useful LCBO approach only includes occupied orbitals and therefore predicts \( n_N^+(a_1) \) above \( n_N^-(b_2) \).

Finally, the NCCCN skeleton orbitals with predominant \( 2s \) character and high ionization energies are considered independent. Their sequence of increasing energy \( 2b_2 > 2a_1 > 1b_2 > 1a_1 \) as determined by the nodal rule is supported by EHMO and CNDO/2 calculations.

**PE-spectrum and assignment**

The He(I)-PE-spectrum of dicyano methane is shown in Fig. 1, expanded records of different bands (cf. experimental section) with assigned vibrational fine structures in Fig. 2 and Fig. 3; the PE-data are summarized in Table I.
highest peak at 13.59 eV is alternatively attributed to either both \( n^-+\) \( (a_1) \) and \( n^-\) \( (b_2) \) orbitals or to \( n^-\) \( (b_2) \) alone, if the \( \sigma (3a_1) \) mixing mentioned before removes the \( n^- \) degeneracy. In the latter case, and regarding the \( n/n \) split of 0.37 eV in cyanogen, the \( n^-\) \( (a_1) \) can only be assigned to the maximum at 13.41 eV; the broader band shape being in agreement with an enhanced \( \sigma \) contribution. Another clearly distinguishable band is the one at 12.68 eV, exhibiting vibrational fine structures \( \nu_{CN}^+ \), \( \nu_{CN} \) and eventually \( \nu_{CH}^+ \) (see Table I and Fig. 2). For this band as well as for the other bands several speculative assignments to the four \( \pi_{CN} \) orbitals (2) are possible. Therefore the following parametrization procedure has been carried out.

We start with the 4 most reasonable sets of ionization potentials and the 6 \( \pi_{CN} \) orbital sequences under the assumptions \( b_2 < a_2 \) and \( b_1 < a_1 \) (2).

<table>
<thead>
<tr>
<th>( IE_v )</th>
<th>A</th>
<th>12.68</th>
<th>12.12</th>
<th>13.41</th>
<th>13.89</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>12.68</td>
<td>12.14</td>
<td>13.89</td>
<td>14.02</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>12.68</td>
<td>12.80</td>
<td>13.41</td>
<td>13.80</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>12.68</td>
<td>12.80</td>
<td>13.14</td>
<td>13.80</td>
</tr>
</tbody>
</table>

Orbital Sequences

<table>
<thead>
<tr>
<th>a</th>
<th>b_1</th>
<th>b_2</th>
<th>a_2</th>
<th>a_1</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>b_1</td>
<td>b_2</td>
<td>a_2</td>
<td>a_1</td>
</tr>
<tr>
<td>c</td>
<td>b_1</td>
<td>b_2</td>
<td>a_1</td>
<td>a_2</td>
</tr>
<tr>
<td>d</td>
<td>b_2</td>
<td>b_1</td>
<td>a_2</td>
<td>a_1</td>
</tr>
<tr>
<td>e</td>
<td>b_2</td>
<td>b_1</td>
<td>a_1</td>
<td>a_2</td>
</tr>
<tr>
<td>f</td>
<td>b_2</td>
<td>a_2</td>
<td>b_1</td>
<td>a_1</td>
</tr>
</tbody>
</table>

The resulting 24 combinations of ionization potentials and \( \pi_{CN} \) orbital sequences are subsequently tested with respect to the following specifications, which relate the six variables \( a_{CN}, \lambda_{\pi}, \Lambda_{\pi}, \sigma, \) \( \lambda_{\pi}, \) \( \sigma(b_2) \) \( \lambda_{\pi}(b_1) \) and \( \lambda_{\pi}(a_1) \) from the MO model (1) and (2) to the PE data:

\[
IE_v(b_2) = -a_{CN} - \frac{1}{2} \lambda_{\pi} - \sigma(b_2) \quad (5)
\]

\[
IE_v(a_2) = -a_{CN} - \frac{1}{2} \lambda_{\pi} + \sigma \quad (6)
\]

\[
IE_v(b_1) = -a_{CN} + \frac{1}{2} \lambda_{\pi} - \sigma(b_1) \quad (7)
\]

\[
IE_v(a_1) = -a_{CN} + \frac{1}{2} \lambda_{\pi} + \sigma(a_1) \quad (8)
\]

This system of Eqns. (5)-(8) contains six variables and only four experimental values. To obtain the lacking two parameters a fixed ratio \( \Lambda_{\pi}/\lambda_{\pi} \) will be introduced and \( \lambda_{\pi} \) chosen as independent variable. As an estimate for the range over which \( \lambda_{\pi} \) has to be varied can be obtained e.g. using the PE data of cyanogen.

\[
\frac{\lambda_{\pi}}{\Lambda_{\pi}} = \frac{S_{\pi}}{S_{\sigma}} = 0.47 \quad (9)
\]

is considered reliable, because inaccuracies in the SLATER type overlap integrals should largely cancel out when divided. An estimate for the range over which \( \lambda_{\pi} \) has to be varied can be obtained e.g. using the PE data of cyanogen.

The first ionization occurs from the \( \pi_{CN}(2b_1) \) orbital. The vibrational fine structures partly overlap with the second band \( \pi_{CN}(4b_2) \) at about 13.1 eV. The nitrogen lone pairs are presumably split in \( n^-\) \( (5a_1) \) and \( n^-\) \( (3b_2) \), predominantly because of the stronger mixing between the \( a_1 \) orbitals, contrary to the proposed \( n/n \) interaction model. At higher energies follow the ionizations from the \( \pi_{CN}(1a_1) \) and \( \pi_{CN}(4a_1) \) orbitals. The above parametriza-
tion yields a consistent orbital sequence in the crowded $\pi_{CN}-n_N$ region, which is only partly reproduced by EHMO and CNDO/2 calculations.

In the $\sigma$ region three bands are observed (Fig. 1 and Tab. I). The first band (Fig. 3) starts at 16.62 eV with a progression of $1280 \pm 80$ cm$^{-1}$, which only can be attributed to a reduced symmetric CH$_2$-deformation. This proves bonding character between the two hydrogens and consequently the assignment to $\sigma(3a_1)$ with predominant CH character. The following bands lack resolved fine structures and according to MO calculations are assigned to the orbitals $\sigma_{CN}(1b_1)$ and $\sigma_{CCN}(2b_2)$.

The assignment of the PE spectrum of dicyano methane was achieved on the basis of the following parameters:

$$a_{CN} = -14.1 \text{ eV} \quad \text{tb}(b_1) = 1.7 \text{ eV}$$
$$\Delta \pi_{\sigma} = 0.5 \text{ eV} \quad \text{tb}(a_1) = 0.6 \text{ eV}$$
$$\Delta \pi_{\alpha} = 1.0 \text{ eV} \quad \text{tb}(b_2) = 0.5 \text{ eV}$$

The $a_{CN}$ value fits in the order of other cyano hydrocarbons (14).

$$\begin{array}{ccc}
\text{NC} & \text{CN} & \text{CN} \\
-13.7^{14} & -14.1 & \\
\text{NC-CN} & \text{NC} & \text{CN} \\
-14.4^2 & -14.5^2 & \\
\end{array}$$

The ratio $\Delta \pi_{\alpha}/\Delta \pi_{\sigma}$, being a function of the angle between the geminal cyano groups, amounts to about 1:2 for tetrahedral geometry. Most interesting is the through bond shift $\text{tb}(b_1)$, which according to our model (3) represents the hyperconjugation between $\pi_{CN}(2b_1)$ and the pseudo $\pi_{CH_2}(1b_1)$ orbitals. The hyperconjugation parameter $\beta_{CH_2/\pi_{CN}}$ defined as

$$\beta_{CH_2/\pi_{CN}} = \frac{a_{2CN}(2b_1)-\varepsilon}{\beta_{CH_2/\pi_{CN}}}$$

is obtained with the PE spectroscopically deduced values (13) and the ionization energies $IE(1b_1)$ and $IE(2b_2)$ from Tab. I:

$$\beta_{CH_2/\pi_{CN}} = -\sqrt{\left[-a_{CN} + \frac{\Delta \pi_{\alpha}}{2} - 12.7\right]} \frac{IE(1b_1)\text{tb}(b_1) - 12.7}{IE(2b_2) - 12.7}$$

$$= -2.5 \text{ eV}$$

### B. 2,2-Dicyano Propane

The 36 valence electrons of 2,2-dicyano propane occupy 18 molecular orbitals, which can be characterized by their LCBO notations and symmetry species assuming $C_{2v}$ conformation of the methyl groups (17). Comparison with the values in brackets, which refer to the additional orbitals relative to dicyano methane (3), facilitate the discussion:

<table>
<thead>
<tr>
<th>MO</th>
<th>$b_2$</th>
<th>$a_2$</th>
<th>$b_1$</th>
<th>$a_1$</th>
<th>$\Sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pi_{CN}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>$n_N$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$\sigma_{CH}$</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>$\sigma_{CCN}$</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>5</td>
<td>2</td>
<td>4</td>
<td>7</td>
<td>18</td>
</tr>
</tbody>
</table>

Summing up, two additional $\sigma$ orbitals $a_1$ and only one of symmetry type $b_2$ should destabilize $n_N+(a_1)$ to a greater extent than $n_N+(b_2)$ and therefore at least maintain the $n_N^+/(n_N^-)$ split. Two more orbitals $b_1$ compared to each a single $\sigma(b_2)$ and $\sigma(a_2)$ will ensure the $\pi_{CN}$ sequence $b_1 < b_2 < a_2$, which has been determined for dicyano methane.

The He(I)-PE-spectrum of 2,2-dicyano propane is shown in Fig. 4 and an expanded record of the region 12.0 eV–14.0 eV in Fig. 5; the ionization potentials are listed in Tab. II.

Fig. 4. He(I)-PE-spectrum of 2,2-dicyano propane.

Fig. 5. Expanded record of the 12.0 eV–14.0 eV region of 2,2-dicyano propane.
Table II. Vertical ionization potentials $IE_v$(eV) of 2,2-dicyano propane.

<table>
<thead>
<tr>
<th>$IE_v$</th>
<th>MO</th>
<th>$C_{2v}$</th>
<th>$IE_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.39</td>
<td>$\pi$CN</td>
<td>$4_{b_1}$</td>
<td>14.42</td>
</tr>
<tr>
<td>12.79</td>
<td>$\pi$CN</td>
<td>$5_{b_2}$</td>
<td>14.80</td>
</tr>
<tr>
<td>13.05</td>
<td>$n$N</td>
<td>$7_{a_1}$</td>
<td>15.16</td>
</tr>
<tr>
<td>13.21</td>
<td>$n$N</td>
<td>$4_{b_2}$</td>
<td>15.54</td>
</tr>
<tr>
<td>13.60</td>
<td>$\pi$CN</td>
<td>$2_{a_2}$</td>
<td>16.12</td>
</tr>
<tr>
<td>13.81</td>
<td>$\pi$CN</td>
<td>$6_{a_1}$</td>
<td>18.0</td>
</tr>
</tbody>
</table>

In the spectrum of 2,2-dicyano propane, $\sigma$ bands are at least close to if not even superimposed on $\pi$ bands. Broadened $\pi$CN and $n$N band structures indicate larger $\sigma$ contributions relative to dicyano methane (Fig. 1 and Fig. 4). The most intense peak at 13.21 eV is again attributed to the $n$N$^*$ combination and the peak at 13.05 eV analogously to the $n$N$^+$ combination (Fig. 5). Following the above reasoning from (17) the first band at 12.39 eV originates from the $\pi$CN(3$b_1$) orbital. Fortunately, there are no uncertainties concerning the positions of the remaining $\pi$CN bands as in dicyano methane (4); the well resolved peaks (Fig. 5) will even lend some credit to the intensity arguments used in the analysis of the complex band structures in Fig. 2. At first sight three assignments seem possible, if $IE(5_{b_2})<IE(2_{a_2})$ is assumed as before (2).

<table>
<thead>
<tr>
<th>$IE_v$(eV)</th>
<th>12.79</th>
<th>13.60</th>
<th>13.81</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>$b_2$</td>
<td>$a_2$</td>
<td>$a_1$</td>
</tr>
<tr>
<td>(b)</td>
<td>$b_2$</td>
<td>$a_1$</td>
<td>$a_2$</td>
</tr>
<tr>
<td>(c)</td>
<td>$a_1$</td>
<td>$b_2$</td>
<td>$a_2$</td>
</tr>
</tbody>
</table>

Assignment (a) is preferred on account of the following arguments: Both electron pair combinations are shifted about 0.3 eV relative to dicyano methane (Tab. I and Tab. II), reflecting the donor properties of the two methyl groups. Therefore an inductive increase of the parameter $\sigma_{CH_3}$ is expected, which should lower the ionization energy of the $\pi$CN(2$a_2$) orbital. To this shift also the through bond destabilization by the additional $\sigma_{CH_3}(1a_2)$ orbital will contribute. Looking at the PE data (Tab. I and Tab. II) only assignment (a) yields 0.29 eV decrease as opposed to only 0.08 eV in the cases (b) and (c).

The rest of the PE spectrum of dimethyl dicyano methane shows an accumulation of hopelessly overlapping bands, mainly due to the methyl group ionizations. As EHMO and CNDO/2 orbital sequences differ considerably and no clear decision can be made as to which of the peaks belongs to vibrational progressions, no interpretation is attempted.

The two methyl groups of 2,2-dicyano propane situated above and below the (NC)$_2$C-plane will not interfer sterically with the cyano groups. Thus it seems reasonable to adopt the values $\Delta\pi_{CH_3}$, $\Delta\pi_{CH_3}$ and the ratio $\Delta\pi_{CH_3}/\Delta\pi$ used in the MO parametrization of dicyano methane. If, in addition, the through bond destabilization $tb(a_2)$ is neglected, 1.7 eV are obtained as a lower limit for hyperconjugation in 2,2-dicyano propane.

Summarizing, the PE spectra of dicyano methane and of its dimethyl derivative supplement each other: The latter clearly displaying two separated $\pi$CN bands on the high energy side of the $n$N$^+$ ionization, while in the parent compound a gap of more than 3 eV not clouded with overlapping $\sigma_{CH_3}$ bands isolates $\pi$CN and $\sigma$ regions (Fig. 6).

Fig. 6. PE ionization potentials of H$_2$C(CN)$_2$ and (H$_3$C)$_2$C(CN)$_2$ and their assignments.

Obviously the assignable orbital sequences resemble each other in both compounds and the hyperconjugative effects – fully observable only in the parent compound – amount to about 1.7 eV.

C. Hyperconjugation in Methane Derivatives H$_2$CX$_2$ and H$_3$CX

Dicyano methane represents a special case of hyperconjugation because the methylene group
interacts with two identical π systems of cylindrical symmetry. This implies $C_2v$ symmetry and a simple MO scheme with an internal reference point, the 1a$_2$ orbital, relative to which hyperconjugation can be evaluated from the splitting of the only two b$_1$ orbitals. All compounds $H_2CX_2$ with e.g. $X = F, Cl, Br, J, C≡CH$ might be treated analogously. For $H_2CBr_2$, $H_2CCl_2$ and $H_2C(CN)_2$ the PE spectroscopically deduced parameters are summarized in Table II.

A comparison of the values $a$ (Table III) shows, that the cyano group is a strong electron withdrawing substituent, and the values $Aa$, that the spatial overlap is only small. Greater values of the through bond shifts $tb(b_1)$ and $tb(b_2)$ (cf. MO scheme (2)) in the halo compounds are due to the additional interactions between the orbitals $n_X$ and $a_{CX}$, whereas in dicyano methane the corresponding $a_{CC}$ orbitals are less effective because of their high ionization potentials ($> 19.2$ eV). Of all such π/σ or $n/σ$ interactions, hyperconjugation $tb(b_1)$ is clearly dominating and increases from dibromo to dicyano methane (cf. Table III).

Obviously, one of the main factors is the decreasing orbital distance $Aa(b_1)$. The ratios $tb(b_1)/Aa(b_1)$ increase from 0.28 in $H_2CBr_2$ and 0.46 in $H_2CCl_2$ to 0.81 in $H_2C(CN)_2$, so that at least in the latter case the hyperconjugation is too large to be treated by the usual second order perturbation model:

$$\beta_{CH_2/X_2} = tb(b_1) \cdot Aa(b_1)$$

(19)

On the other hand, the $\beta^2$ values derived from (15)

$$\beta_{CH_2/X_2}^2 = \{ax_2(b_1) - \varepsilon\} \cdot \{a_{CH_2}(b_1) - \varepsilon\}$$

$$= tb(b_1) \cdot \{ax_2(b_1) + Aa - \varepsilon\}$$

$$= tb(b_1) \cdot Aa^2 + tb(b_1)^2$$

(20)

are greater by $tb(b_1)^2$, which is an essential difference especially for ratios $tb(b_1)/Aa(b_1) >> 0$. The $\beta$ values (20) determined in the interpretation of PE spectra are rather large (cf. Table III) compared to usual π/σ interactions, but nevertheless are the most typical parameters for hyperconjugation. Within chemically related compounds, i.e. those with comparable geometries and only modest substituent effects, transferability of the parameter $\beta$, is expected. Accordingly, hyperconjugation in methyl bromide can be estimated by

$$\beta_{CH_2/Br} = \sqrt{2} \cdot \beta_{CH_2/Br}$$

(21)

$\sqrt{2}$ simply being the necessary normalization factor. If only two ionization potentials are available but three parameters unknown ($ax, a_{CH_3}$ and $\beta_{CH_3/X}$) such a $\beta$ transfer may help to solve the problem. The procedure is illustrated in Fig. 7.

The $H_2CX$ ionization energies $IE(X)$ (eV) and estimated MO parameters $a$ (eV) of methane derivatives $H_2CX_2$ and $H_3CX$ with $X = Br, Cl, CN$.

$$\alpha_{X, CH_3} = \frac{IE(2e) + IE(1e)}{2} \pm \sqrt{\left(\frac{IE(2e) - IE(1e)}{2}\right)^2 - \beta_{CH_3/X}^2}$$

(22)
which is also easily obtained from (15). The \( \alpha \) values for \( \text{H}_2\text{CB} \) and \( \text{H}_2\text{CC} \) are listed in Table IV. For \( \text{H}_2\text{CCN} \) the radicand becomes negative. This shows, that \( \beta_{\text{CH}_3/X} \) from \( \text{H}_3\text{(CN)}_2 \) is too large to be transferred to \( \text{H}_2\text{CCN} \). Therefore we assume \( \alpha_{\text{CH}_3} = -14.5 \text{ eV} \) (Table IV and Fig. 7) as an upper limit and calculate from the two ionization energies \( IE(1e) \) and \( IE(2e) \) of \( \text{H}_2\text{CCN} \) the maximum values of \( \alpha_{\text{CN}} \) and \( \beta_{\text{CH}_3\text{CN}} \) (Table IV).

Table IV. Ionization energies\(^a\) and estimated MO parameters (eV) for \( \text{H}_3\text{CX} \) with \( X = \text{Br}, \text{Cl}, \text{CN} \).

<table>
<thead>
<tr>
<th>( X )</th>
<th>( 2e )</th>
<th>( 1e )</th>
<th>( \beta_{\text{CH}_3/X} )</th>
<th>( \alpha_X )</th>
<th>( \alpha_{\text{CH}_3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Br} )</td>
<td>10.7</td>
<td>15.1</td>
<td>-1.6</td>
<td>-11.3</td>
<td>-14.5</td>
</tr>
<tr>
<td>( \text{Cl} )</td>
<td>11.3</td>
<td>15.3</td>
<td>-1.6</td>
<td>-12.1</td>
<td>-14.5</td>
</tr>
<tr>
<td>( \text{CN} )</td>
<td>12.2</td>
<td>15.5</td>
<td>-1.5*</td>
<td>-13.2*</td>
<td>-14.5*</td>
</tr>
</tbody>
</table>

* With \( \alpha_{\text{CH}_3} \) assumed.

It should be mentioned at this point, that an assignment of the band at 17.3 eV in dicyano methane to the orbital \( 1b_1 \) would yield \( \beta_{\text{CH}_2\text{CN}} = -2.2 \text{ eV} \) and \( \beta_{\text{CH}_2\text{CN}} = -1.6 \text{ eV} \) in good agreement with the estimated maximum values (Tab. IV). Although the resolved vibrational fine structures rather suggest an assignment to the \( a_1 \) orbital, the alternate possibility can not be excluded.

Summarizing, hyperconjugation models as illustrated for \( \text{H}_2\text{CX}_2 \) and \( \text{H}_2\text{CX} \) are useful in the interpretation of PE spectra. Nevertheless there seem to be several restrictions, e.g. the limited transferability of the astonishingly large \( \beta \) values.

D. Experimental Section

Dicyano methane (MERCK) was recrystallized from ether, 2,2-dicyano propane prepared from the di-silver salt of dicyano methane and methyl iodide\(^{14}\) and purified by vacuum sublimation.

The PE spectra were recorded on a PERKIN-ELMER PS 16 and calibrated using the argon peaks (half width 20-25 meV); all data reported are mean values of several measurements. Ionization potentials refer to band maxima or to the maximum of the highest peak, if vibrational fine structures are resolved. As the first peak coincides with the first ionization potential of water, gaseous dicyano methane was passed through phosphorous pentoxide before entering the PE spectrometer. Furthermore, no water was detected in the mass spectrum and the IR spectrum of the sample. Elemental analysis yielded sums of 99.2% and 98.9% of C, H and N.

The EHMO and CNDO/2 calculations were performed on the UNIVAC 1108 of the Zentrales Recheninstitut of the University of Frankfurt.

The mass spectrum was recorded on a VARIAN 457.

Elemental analysis were performed by the analytical laboratory of the Farbwere Hoechst A.G.