

Photoelectron Spectra and Molecular Properties. XVII¹**Hyperconjugation in Dicyano Methane and 2,2-Dicyano Propane²**

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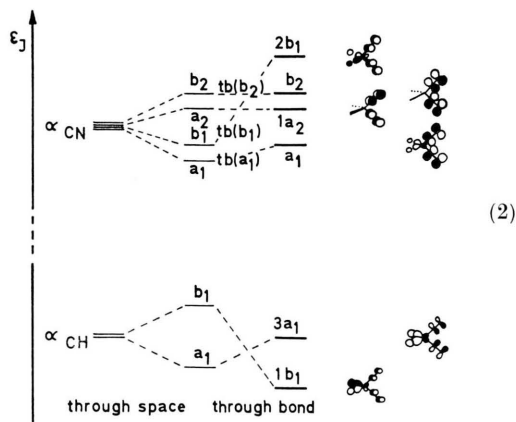
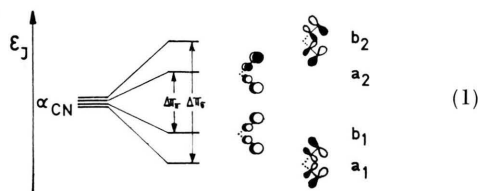
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Photoelectron spectra, hyperconjugation, methylene derivatives

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 R₂C-framework can be parametrized using the PE data. Thus the hyperconjugation $\pi_{\text{CN}}/\pi_{\text{CR}_2}$ is estimated to amount to 1.7 eV in both compounds. Hyperconjugative effects in methane derivatives H₃CX and H₂CX₂ with X = Br, Cl and CN are compared.

Neighbouring cyano groups loose their cylindrical symmetry in molecules of C_{2v} symmetry by "through space" interaction:



Additional "through bond" interactions (2) with σ orbitals of the same irreducible representations destabilize all orbitals except 1a₂, which therefore might serve as an internal standard in dicyano methane.

The applicability of this simple model to compounds R₂C(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).

C _{2v}						
MO	b ₂	a ₂	b ₁	a ₁	Σ	
π _{CN}	1	1	1	1	4	
n _N	1	—	—	1	2	
σ _{CH}	—	—	1	1	2	
σ _{CCN}	2	—	—	2	4	
Σ	4	1	2	5	12	(3)

Mixing of all symmetry equivalent basis orbitals according to their overlap and energy differences yields molecular orbitals, which may be classified as π , σ and n_N .

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The systems in and perpendicular to the molecular plane are formed mainly from the orbitals π_{CN} and σ_{CH} . The symmetry controlled π/σ 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 π/σ 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 π orbital b_2 lies above a_2 , and b_1 probably³ above a_1 . Other sequences remain uncertain. Assuming validity of KOOPMANS theorem⁴ the MO model (2) helps in assigning the PE spectrum.

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

According to the n/n interaction model by HOFFMANN, IMAMURA, and HEHRE⁶ both the $n_{\text{N}}^-(b_2)$ and $n_{\text{N}}^+(a_1)$ combinations should be destabilized by through bond interactions to approximately the same extent, because of the even number of intervening σ 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 $n_{\text{N}}^+(a_1)$ above $n_{\text{N}}^-(b_2)$.

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.

Fig. 1. He(I)-PE-spectrum of dicyano methane.

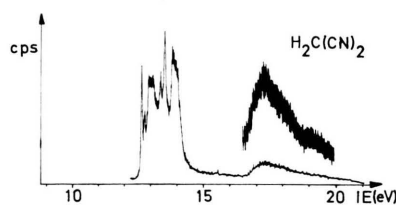


Fig. 2. Expanded record of the π_{CN} bands (12.5 eV–14.5 eV) of dicyano methane with assigned vibrational fine structures and orbitals.

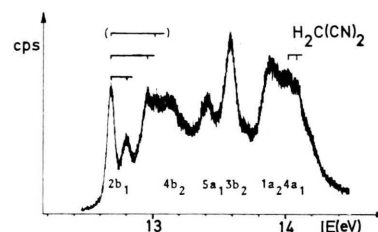


Fig. 3. Expanded record of the σ_{CH} bands (16.0 eV–19.0 eV) of dicyano methane with assigned vibrational fine structures and orbitals.

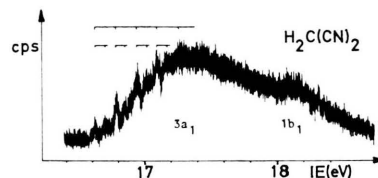


Table I. Vertical PE-ionization potentials IE_{v} (eV) of dicyano methane (see text) and comparison of assigned vibrational frequencies ν^+ (cm^{-1}) of the molecular cation states with those of the ground state (ν).

IE_{v}	MO	$\text{C}_{2\text{v}}$	ν^+	ν^{\ddagger}	vibrational mode ⁷
12.68	π_{CN}	$2b_1$	2800	2951	C–H stretch)
			2200	2274	C \equiv N stretch
			960	892	C–C stretch
13.1	π_{CN}	$4b_2$			
13.41	n_{N}^+	$5a_1$			
13.59	n_{N}^-	$3b_2$			
13.89	π_{CN}	$1a_2$			
14.02	π_{CN}	$4a_1$	480	582	C–C–C bend
17.28	σ_{CH}	$3a_1$	1280	1422	CH_2 deformation
			800	892	C–C stretch
18.1	σ_{CH}	$1b_1$			
19.1	σ	$2b_2$			

Meeting the expectations from the orbital construction, the PE spectrum of dicyano methane shows separated π_{CN} , n_{N} and σ band regions:

π_{CN} and n_{N} ionizations lead to the complex band structures between 12.5 eV and 14.5 eV. The

highest peak at 13.59 eV is alternatively attributed to either both $n_N^+(a_1)$ and $n_N^-(b_2)$ orbitals or to $n_N^-(b_2)$ alone, if the σ ($3a_1$) mixing mentioned before removes the n_N degeneracy. In the latter case, and regarding the n/n split of 0.37 eV in cyanogen⁸, the $n_N^+(a_1)$ can only be assigned to the maximum at 13.41 eV; the broader band shape being in agreement with an enhanced σ contribution. Another clearly distinguishable band is the one at 12.68 eV, exhibiting vibrational fine structures ν_{CN}^+ , ν_{CC}^+ and eventually ν_{CH}^+ (see Table I and Fig. 2). For this band as well as for the other bands several speculative assignments to the four π_{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 π_{CN} orbital sequences under the assumptions $b_2 < a_2$ and $b_1 < a_1$ (2).

IE_V	A	12.68	13.12	13.41	13.89
	B	12.68	13.14	13.89	14.02
	C	12.68	12.89	13.41	13.89
	D	12.68	12.89	13.14	13.89
Orbital Sequences	a	b_1	b_2	a_2	a_1
	b	b_1	b_2	a_1	a_2
	c	b_1	a_1	b_2	a_2
	d	b_2	b_1	a_2	a_1
	e	b_2	b_1	a_1	a_2
	f	b_2	a_2	b_1	a_1

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

$$IE_V(b_2) = -a_{CN} - \frac{1}{2} \Delta\pi_\sigma - tb(b_2) \quad (5)$$

$$IE_V(a_2) = -a_{CN} - \frac{1}{2} \Delta\pi_\pi \quad (6)$$

$$IE_V(b_1) = -a_{CN} + \frac{1}{2} \Delta\pi_\pi - tb(b_1) \quad (7)$$

$$IE_V(a_1) = -a_{CN} + \frac{1}{2} \Delta\pi_\sigma - tb(a_1) \quad (8)$$

This system of Eqns. (5)–(8) contains six variables and only four experimental values. To obtain the lacking two parameters a fixed ratio $\Delta\pi_\pi/\Delta\pi_\sigma$ will be introduced and $\Delta\pi_\pi$ chosen as independent variable. As an approximation⁹, the overlap ratio

$$\frac{\Delta\pi_\pi}{\Delta\pi_\sigma} \equiv \frac{S_\pi}{S_\sigma} = 0.47 \quad (9)$$

is considered reliable, because inaccuracies in the SLATER type overlap integrals should largely cancel out when divided. An estimate for the range over which $\Delta\pi_\pi$ has to be varied can be obtained *e.g.* using the PE data of cyanogen⁸

$$\Delta\pi_\pi^{CH_2(CN)_2} = \Delta\pi_\pi^{NCCN} \cdot \frac{S_\pi^{CH_2(CN)_2}}{S_\pi^{NCCN}} \approx 0.3 \text{ eV} \quad (10)$$

or that of tetracyano methane² yielding⁹ $\Delta\pi_\pi \approx 0.5$ eV. Therefore $\Delta\pi_\pi$ was varied stepwise by 0.05 eV from 0.3 eV to 0.5 eV for all 24 combinations (4) and the values a_{CN} , $\Delta\pi_\sigma$, $tb(b_2)$, $tb(b_1)$ and $tb(a_1)$ were calculated from Eqns. (5)–(8). If then, according to EHMO or CNDO/2 calculations increasing through bond shifts (see diagram (2))

$$0 < tb(b_2) < tb(a_1) < tb(b_1) \quad (11)$$

are assumed, 12 of the combinations are eliminated.

In 9 other combinations the broad band complex between 13.8 eV and 14.2 eV (Fig. 2) is assigned solely to the ionization from the orbital $\pi_{CN}(1a_2)$. Being incompatible both with the expected π band shape¹⁰ and the expected vibrational fine structure, there remain only 3 acceptable assignments.

	I	II	III	
b_1	12.68	12.68	12.68	(eV)
b_2	13.1	13.1	13.1	(eV)
a_2	13.89	14.02	13.41	(eV)
a_1	14.02	13.89	13.89	(eV)

I to III differ only in the sequence a_2/a_1 (II and ionization potentials n_N/π_{CN} (III; *cf.* (12) dotted line). Although intensity arguments in the assignment of PE spectra are of limited importance^{4b}, the expanded record in Fig. 2 clearly shows, that out of six ionizations in the whole band complex two have to be attributed to its intense high energy flank ≥ 13.8 eV. After the exclusion of III the final assignment I given in Tab. I rests on the following assumptions: The reduced CCC-bending frequency $\nu^+ = 480 \pm 80 \text{ cm}^{-1}$ at 14.02 eV suggests the sequence $\pi_{CN}(1a_2) < \pi_{CN}(4a_1)$. For the peak at 13.41 eV an assignment to $n_N^+(5a_1)$ – implying non degenerate nitrogen lone pairs – is preferred to a vibrational progression from the $\pi_{CN}(4b_2)$ band.

Thus the parametrization of the π_{CN}, n_N complex combined with the discussion of vibrational fine structures, band shapes, and intensities leads to the assignment given in Fig. 2 and Tab. I: 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 $n_N^+(5a_1)$ and $n_N^-(3b_2)$, predominantly because of the stronger mixing between the a_1 orbitals, contrary to the proposed n/n interaction model⁶. At higher energies follow the ionizations from the $\pi_{CN}(1a_2)$ and $\pi_{CN}(4a_1)$ orbitals. The above parametriza-

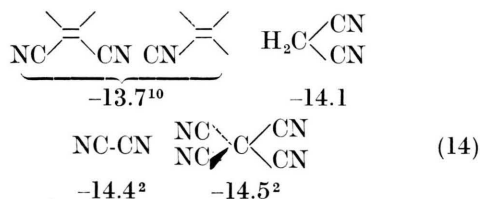
tion yields a consistent orbital sequence in the crowded $\pi_{\text{CN}}, n_{\text{N}}$ region, which is only partly reproduced by EHMO and CNDO/2 calculations.

In the σ region three bands are observed (Fig. 1 and Tab. I). The first band (Fig. 3) starts at 16.62 eV with a progression of $1280 \pm 80 \text{ cm}^{-1}$, 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 $\sigma_{\text{CN}}(1b_1)$ and $\sigma_{\text{CCN}}(2b_2)$.

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

$$\begin{aligned} a_{\text{CN}} &= -14.1 \text{ eV} & \text{tb}(b_1) &= 1.7 \text{ eV} \\ \Delta\pi_{\pi} &= 0.5 \text{ eV} & \text{tb}(a_1) &= 0.6 \text{ eV} \\ \Delta\pi_{\sigma} &= 1.0 \text{ eV} & \text{tb}(b_2) &= 0.5 \text{ eV} \end{aligned} \quad (13)$$

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



The ratio $\Delta\pi_{\pi}/\Delta\pi_{\sigma}$, being a function of the angle between the geminal cyano groups², 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 $\pi_{\text{CN}}(2b_1)$ and the pseudo $\pi_{\text{CH}_2}(1b_1)$ orbitals. The hyperconjugation parameter $\beta_{\text{CH}_2/2\text{CN}}$ defined as

$$\left\| \begin{array}{cc} a_{2\text{CN}}(2b_1) - \epsilon & \beta_{\text{CH}_2/2\text{CN}} \\ \beta_{\text{CH}_2/2\text{CN}} & a_{\text{CH}_2}(1b_1) - \epsilon \end{array} \right\| \quad (15)$$

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

$$\begin{aligned} \beta_{\text{CH}_2/2\text{CN}} &= -\sqrt{\frac{[-a_{\text{CN}} + \frac{\Delta\pi_{\pi}}{2}] - 12.7}{\text{tb}(b_1) - 12.7}} [IE(1b_1) - 12.7] \\ &= -2.5 \text{ eV} \end{aligned} \quad (16)$$

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:

MO	C_{2v}				
	b_2	a_2	b_1	a_1	Σ
π_{CN}	1	1	1	1	4
n_{N}	1	—	—	1	2
σ_{CH}	1	1	2	2	6
	(1)	(1)	(1)	(1)	(4)
$\sigma_{\text{CC}}, \sigma_{\text{CN}}$	2	—	1	3	6
			(1)	(1)	(2)
Σ	5	2	4	7	18
	(1)	(1)	(2)	(2)	(6)

Summing up, two additional σ orbitals a_1 and only one of symmetry type b_2 should destabilize $n_{\text{N}}+(a_1)$ to a greater extent than $n_{\text{N}}-(b_2)$ and therefore at least maintain the $n_{\text{N}}+/n_{\text{N}}^-$ split. Two more orbitals b_1 compared to each a single $\sigma(b_2)$ and $\sigma(a_2)$ will ensure the π_{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.

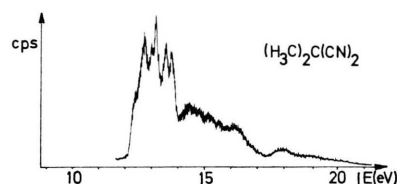


Fig. 4. He(I)-PE-spectrum of 2,2-dicyano propane.

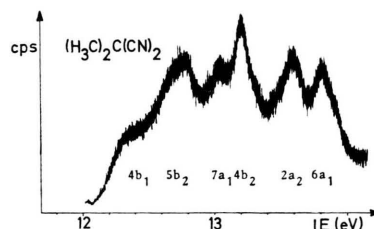


Fig. 5. Expanded record of the 12.0 eV–14.0 eV region of 2,2-dicyano propane.

Table II. Vertical ionization potentials IE_V (eV) of 2,2-dicyano propane.

IE_V	MO	C_{2v}	IE_V	MO
12.39	π_{CN}	$4b_1$	14.42	} σ
12.79	π_{CN}	$5b_2$	14.80	
13.05	n_N	$7a_1$	15.16	
13.21	n_N	$4b_2$	15.54	
13.60	π_{CN}	$2a_2$	16.12	
13.81	π_{CN}	$6a_1$	18.0	
			19.0	

In the spectrum of 2,2-dicyano propane, σ bands are at least close to if not even superimposed on π bands. Broadened π_{CN} and n_N band structures indicate larger σ 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 $\pi_{CN}(3b_1)$ orbital. Fortunately, there are no uncertainties concerning the positions of the remaining π_{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 $IE(5b_2) < IE(2a_2)$ is assumed as before (2).

IE_V (eV)	12.79	13.60	13.81	
(a)	b_2	a_2	a_1	(18)
(b)	b_2	a_1	a_2	
(c)	a_1	b_2	a_2	

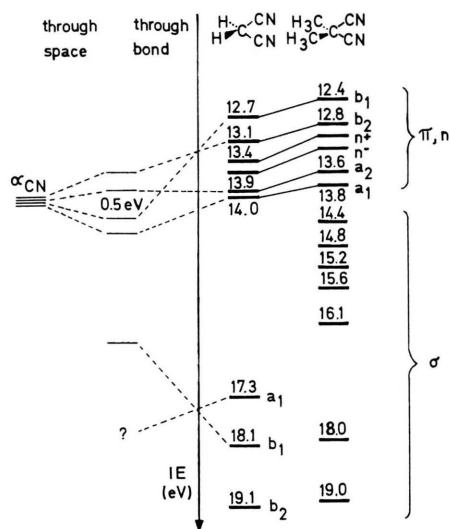
Assignment (a) is preferred on account of the following arguments: Both electron pair combinations are shifted about 0.3 eV relative to dicyano methane (Tab. I and Tab. II), reflecting the donor properties of the two methyl groups. Therefore an inductive increase of the parameter α_{CN} is expected, which should lower the ionization energy of the $\pi_{CN}(2a_2)$ 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 $(NC)_2C$ -plane will not interfere sterically with the cyano groups. Thus it seems reasonable to adopt the values $\Delta\pi\pi$, $\Delta\pi\sigma$ and the ratio $\Delta\pi\pi/\Delta\pi\sigma$ 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 π_{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 σ_{CH_3} bands isolates π_{CN} and σ regions (Fig. 6).

Fig. 6. PE ionization potentials of $H_2C(CN)_2$ and $(H_3C)_2C(CN)_2$ 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_2CX_2 and H_3CX

Dicyano methane represents a special case of hyperconjugation because the methylene group

Table III. MO parameters (eV) for methylene compounds H_2CX_2 with $X = Br, Cl, CN$ evaluated from their PE spectra.

X	α_X	$\Delta\sigma$	$\Delta\pi$	tb(a_1)	tb(b_2)	tb(b_1)	$\alpha_{X_2}(b_1)$	$\alpha_{CH_2}(b_1)$	$\Delta a(b_1)$	β_{CH_2/X_2}
Br*	-11.5	1.2	0.4	0.7	0.8	1.00	-11.7	-15.3	3.6	-2.13
Cl*	-12.5	1.3	0.5	0.9	1.0	1.30	-12.7	-15.5	2.8	-2.30
CN	-14.1	1.0	0.5	0.6	0.5	1.71	-14.4	-16.4	2.1	-2.52

* Parameters from ref. 9; calculation of $\alpha_{X_2}(b_1)$, $\alpha_{CH_2}(b_1)$ and β_{CH_2/X_2} based on PE data from ref. 12.

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.* $X = F, Cl, Br, J, C\equiv CH$ 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 III.

A comparison of the values α (Table III) shows, that the cyano group is a strong electron withdrawing substituent, and the values $\Delta\sigma$, that the spatial overlap is only small. Greater values of the through bond shifts $tb(a_1)$ and $tb(b_2)$ (*cf.* MO scheme (2)) in the halo compounds are due to the additional interactions between the orbitals n_X and σ_{CX} , whereas in dicyano methane the corresponding σ_{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 $\Delta a(b_1)$. The ratios $tb(b_1)/\Delta a(b_1)$ 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:

$$\beta_{CH_2/X_2}^2 = tb(b_1) \cdot \Delta a(b_1) \quad (19)$$

On the other hand, the β^2 values derived from (15)

$$\begin{aligned} \beta_{CH_2/X_2}^2 &= \{\alpha_{X_2}(b_1) - \varepsilon\} \cdot \{\alpha_{CH_2}(b_1) - \varepsilon\} \\ &= tb(b_1) \cdot \{\alpha_{X_2}(b_1) + \Delta a - \varepsilon\} \\ &= tb(b_1) \cdot \Delta a^2 + tb(b_1)^2 \end{aligned} \quad (20)$$

are greater by $tb(b_1)^2$, which is an essential difference especially for ratios $tb(b_1)/\Delta a(b_1) \gg 0$. The β values (20) determined in the interpretation of PE spectra are rather large (*cf.* Table III) compared

to usual π/π interactions^{10,11}, 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 parameters β , is expected. Accordingly, hyperconjugation in methyl bromide can be estimated by

$$\beta_{CH_2/Br_2} = \sqrt{2} \cdot \beta_{CH_3/Br} \quad (21)$$

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

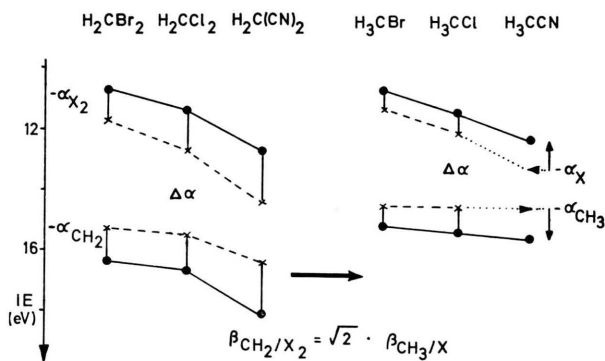


Fig. 7. Ionization energies IE_V (eV) and estimated MO parameters $-\alpha$ (eV) of methane derivatives H_2CX_2 and H_3CX with $X = Br, Cl, CN$.

The H_3CX ionization energies $IE(1e)$ and $IE(2e)$ together with the transferred $\beta_{CH_3/X}$ allow to determine the corresponding values α_X and α_{CH_3} by Eqn. (22)

$$\begin{aligned} \alpha_{X, CH_2} &= -\frac{IE(2e) + IE(1e)}{2} \pm \\ &\sqrt{\left(\frac{IE(2e) - IE(1e)}{2}\right)^2 - \beta_{CH_3/X}^2} \end{aligned} \quad (22)$$

which is also easily obtained from (15). The α values for H_3CBr and H_3CCl are listed in Table IV. For H_3CCN the radicand becomes negative. This shows, that $\beta_{\text{CH}_3/\text{X}_2}$ from $\text{H}_2\text{C}(\text{CN})_2$ is too large to be transferred to H_3CCN . Therefore we assume $\alpha_{\text{CH}_3} = -14.5$ eV (Table IV and Fig. 7) as an upper limit and calculate from the two ionization energies $IE(1e)$ and $IE(2e)$ of H_3CCN the maximum values of α_{CN} and $\beta_{\text{CH}_3/\text{CN}}$ (Table IV).

Table IV. Ionization energies¹³ and estimated MO parameters (eV) for H_3CX with X = Br, Cl, CN.

X	2e	1e	$\beta_{\text{CH}_3/\text{X}}$	α_{X}	α_{CH_3}
Br	10.7	15.1	-1.5	-11.3	-14.5
Cl	11.3	15.3	-1.6	-12.1	-14.5
CN	12.2	15.5	-1.5*	-13.2*	-14.5*

* With α_{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 $\beta_{\text{CH}_2/\text{CN}} = -2.2$ eV and $\beta_{\text{CH}_3/\text{CN}} = -1.6$ 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 H_2CX_2 and H_3CX are useful in the interpretation of PE spectra. Nevertheless there seem to be several restrictions, *e.g.* the limited transferability of the astonishingly large β 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 iodide¹⁴ 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 CH 7, the IR spectrum on a PERKIN-ELMER 457.

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

¹ Communication XVII, K. WITTEL, A. HAAS and H. BOCK. Chem. Ber., **105**, 3865 (1972).

² H. STAFAST, part of thesis, University of Frankfurt 1974.

³ EHMO and CNDO/2 calculations yield $tb(b_1) > tb(a_1) > tb(b_2) > 0$ and the π orbital sequences $b_1 > a_1$ and $b_2 > a_2$.

⁴ a) T. KOOPMANS, Physica **1**, 104 [1934].

b) C. R. BRUNDLE and M. B. ROBIN, "Photoelectron Spectroscopy" in: "Determination of Organic Structures by Physical Methods" **3**, 1 [1971] ed. by F. C. NACHOD and J. J. ZUCKERMANN, Academic Press, New York/London 1971.

c) F. BROGLI, P. A. CLARK, E. HEILBRONNER, and M. NEUENSCHWANDER, Angew. Chem. **85**, 414 [1973]; intern. Edit. **12**, 422 [1973].

⁵ F. FREEMAN, Chem. Rev. **69**, 592 [1969].

⁶ R. HOFFMANN, A. IMAMURA and W. J. HEHRE, J. Amer. chem. Soc. **90**, 1499 [1968].

⁷ F. HALVERSON and R. J. FRANCE, J. chem. Physics **17**, 694 [1949].

⁸ C. BAKER and D. W. TURNER, Proc. Roy. Soc. A [London], Ser. A, **308**, 19 [1968].

⁹ R. N. DIXON, J. N. MURRELL, and B. NARAYAN, Molecular Physics **20**, 611 [1971].

¹⁰ H. BOCK and H. STAFAST, Chem. Ber. **105**, 1158 [1972].

¹¹ H. BOCK and K. WITTEL, Chem. Commun. **1972**, 603.

¹² A. W. POTTS, H. J. LEMPKA, D. G. STREETS, and W. C. PRICE, Phil. Trans. Roy. Soc. [London], Ser. A, **268**, 59 [1970].

¹³ D. W. TURNER, C. BAKER, A. D. BAKER, and C. R. BRUNDLE, Molecular Photoelectron Spectroscopy, Wiley Interscience, London/New York/Toronto 1970.

¹⁴ B. C. HESSE, Amer. chem. J. **18**, 729 [1896].