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## Electronic Structures and Spectra of Cyanoethylene Derivatives

By

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Results of two different types of molecular orbital calculations of several  $\pi$ -orbital systems containing nitrile groups are reported and compared. The bidentate ligand *bis*-(methyl-mercapto)maleonitrile and related molecules are included. Electronic spectra of these molecules are reported and assigned in terms of the calculated energies.

Nach zwei verschiedenen Näherungen werden im Rahmen der Methode der Molekülbahnen die  $\pi$ -Elektronenzustände einiger Moleküle, die Nitrilgruppen enthalten, untersucht. Es werden der zweizählige Ligand 2,3-Bis-methylmercapto-maleinsäuredinitril und verwandte Moleküle betrachtet. Die Elektronenspektren dieser Verbindungen lassen sich mit Hilfe der berechneten Termenergien deuten.

Pour quelques systèmes aux électrons  $\pi$  et possédant des groupes CN, y compris le ligande chélatant NC-C(SCH<sub>3</sub>)-C(SCH<sub>3</sub>)-CN et de molécules semblables, nous donnons et comparons les résultats de deux variantes de la méthode des orbitales moléculaires. Les spectres électroniques de ces molécules sont donnés et interprétés à l'aide des énergies calculées.

### Introduction

Of late, the chemistry of *bis*-mercaptomaleonitrile (mnt) has assumed proportions in the field of inorganic chemistry that make an analysis of its basic electronic structure particularly important. Its ability to form square-planar complexes with a host of transition metal cations marks it as a ligand which will receive increasing attention in the future [8]. In investigating the electronic structure of mnt it was found most convenient to work with the dimethyl thioether. Tetrahedral carbon effectively caps the ends of the  $\pi$ -system without appreciably disturbing the delocalized  $\pi$ -electronic structure. The dimethyl derivative also is more stable chemically than mnt itself.

This paper presents an analysis of the electronic absorption spectra of the dimethyl derivative of mnt and several related molecules in terms of molecular orbital theory.

### Results

Two types of calculations were carried out; a set of calculations including the overlap integrals and a set of standard Hückel calculations. In both sets, only the  $p_{\pi}$ -systems were treated, since the filled  $\sigma$ -orbitals are probably too stable to give rise to electronic transitions in the energy range studied ( $< 53,000 \text{ cm}^{-1}$ ). The molecular orbitals were of the form  $\psi = \sum c_i p_{\pi i}$  where the  $c_i$ 's are subjected to the usual conditions of normalization and orthogonality.

#### *a) Hückel (HMO) calculations*

In this set of calculations, the standard Hückel approximations were assumed ( $S_{ij} = \delta_{ij}$ ,  $\beta_{ij} = 0$  if  $|i - j| > 1$ ). Preliminary values of the molecular parameters

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were chosen from the literature [11] and then adjusted to give the best possible agreement with the experimental results. The following values were found to be consistent with the electronic spectral data:

$$\begin{aligned} \alpha_{\text{C}} &= \alpha & \beta_{\text{C-C}} &= \beta & \beta &= -31,000 \text{ cm}^{-1} \\ \alpha_{\text{S}} &= \alpha + .4 \beta & \beta_{\text{C-N}} &= 1.8 \beta \\ \alpha_{\text{N}} &= \alpha + .6 \beta & \beta_{\text{C-S}} &= .6 \beta \\ & & \beta_{\text{C-CN}} &= .8 \beta . \end{aligned}$$

In the Hückel approximation, the electronic population is given by:

$$\text{Pop}_{j \text{ th atom}} = \sum_{\substack{\text{all occupied} \\ \text{levels}}} a c_j^2 \quad a = 1, 2 .$$

### b) Calculations including overlap integrals (OMO)

For this set of calculations, the overlaps were evaluated explicitly and the resonance integrals were assumed to be proportional to overlap integrals.

The overlaps were calculated by the usual procedure [1] using Clementi's [3] double-zeta basis functions and bond lengths obtained from the literature [4, 7]. Both HMO and OMO calculations were performed using programs written for the Columbia IBM-7094 computer. The procedure used for the OMO calculations has been described in detail elsewhere [1, 2].

The resonance integrals were calculated according to the formula

$$H_{ij} = \sqrt{H_{ii} H_{jj}} (-F S_{ij})$$

where the  $S_{ij}$ 's are the overlap integrals and the  $H_{ii}$ 's and  $H_{jj}$ 's are estimated as valence orbital ionization potentials (VOIP). The VOIP have been tabulated [1, 2]. The value  $F = 2.3$  was used for all  $H_{ij}$ .

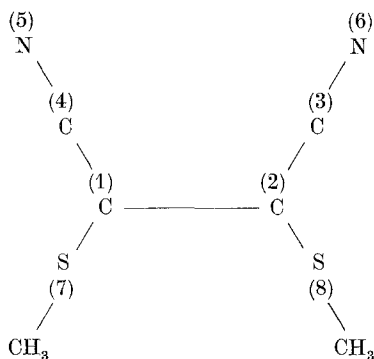
In these calculations the population analysis is given by the formula:

$$\text{Pop}_{j \text{ th atom}} = \sum a c_j^2 + \sum a c_j c_i S_{ij} .$$

### Discussion

We now compare the results of these calculations on various molecules with the spectra given in Tab. 1. The eigenvectors are given in Appendix I.

*Bis-(methylmercapto)maleonitrile* [(CH<sub>3</sub>)<sub>2</sub>mnt]. The system for this molecule (C<sub>2v</sub>) is labeled as follows:



(CH<sub>3</sub>)<sub>2</sub> mnt

Table 1. *Electronic Absorption Spectra of Several Molecules Containing Nitrile Groups*

Molecule	Solvent	$\tilde{\nu}_{\max}$ cm <sup>-1</sup> ( $\epsilon$ )
Bis-(methylmercapto)-maleonitrile	C <sub>2</sub> H <sub>5</sub> OH	43,240 (5,370); 35,971 (5,300); 29,326 (16,000);
	CH <sub>3</sub> OH	45,420 (6,000); 36,790 (5,700); 29,460 (15,900)
Bis-(methylmercapto)-fumaronitrile	CH <sub>3</sub> OH	46,840 (5,600); 36,630 (4,100); 29,350 (11,900)
Tetracyanoethylene	C <sub>2</sub> H <sub>5</sub> OH	40,733 (10,080); 24,014 (sh.) (2,400)
	CH <sub>3</sub> OH	40,520 (11,800)
Fumaronitrile <sup>a</sup>	C <sub>2</sub> H <sub>5</sub> OH	45,450 (15,880)
Maleonitrile <sup>a</sup>	C <sub>2</sub> H <sub>5</sub> OH	45,450 (14,480)
Acrylonitrile	C <sub>2</sub> H <sub>5</sub> OH	51,800 (10,000); 48,500 (sh.)

<sup>a</sup> From ref. [12].

The energies calculated by both procedures are given in Tab. 2. It should be noted that both calculations gave the same ordering of molecular orbital levels.

The first band, centered at 29,326 cm<sup>-1</sup> (EtOH), is fairly intense ( $\epsilon = 16,000$ ), and both calculations attribute this band to the allowed transition  $3 b_1 \rightarrow 3 a_2$  [ ${}^1A_1 \rightarrow {}^1B_2$ ]. The HMO scheme predicts the transition at  $.90 \beta$  or ca. 27,900 cm<sup>-1</sup> whereas the OMO calculation predicts the transition at 27,725 cm<sup>-1</sup>. Both calculations are in good agreement with experiment. The calculations predict another allowed band in the range of the spectrophotometer. The HMO calculation gives a transition  $2 a_2 \rightarrow 3 a_2$  [ ${}^1A_1 \rightarrow {}^1A_1$ ] at  $\Delta = 1.46 \beta$  or 45,260 cm<sup>-1</sup>. In the OMO procedure, the transition  $2 a_2 \rightarrow 3 a_2$  is predicted at 53,070 cm<sup>-1</sup>. Hence the band at

Table 2. *Energies and Symmetry Properties of the  $\pi$ -Molecular Orbitals of Bis-(Methylmercapto) maleonitrile*

MO	HMO energy	OMO energy (cm <sup>-1</sup> )
1 $b_1$	$\alpha + 2.37 \beta$	- 135,857
1 $a_2$	$\alpha + 2.22 \beta$	- 132,764
2 $b_1$	$\alpha + 1.25 \beta$	- 120,375
2 $a_2$	$\alpha + 0.62 \beta$	- 104,487
3 $b_1$	$\alpha + 0.06 \beta$	- 79,142
3 $a_2$	$\alpha - 0.84 \beta$	- 51,417
4 $b_1$	$\alpha - 1.68 \beta$	57,118
4 $a_2$	$\alpha - 2.00 \beta$	127,991

45,420 cm<sup>-1</sup> is assigned  $2 a_2 \rightarrow 3 a_2$ , and it is interesting that the HMO method gives better agreement with experiment. The band observed in EtOH at 35,971 cm<sup>-1</sup> ( $\epsilon = 5300$ ) probably derives a good fraction of its intensity from the strong band at 29,326 cm<sup>-1</sup>. This is assigned as a "perpendicular"  $n \rightarrow \pi^*$ -type transition from an inplane sulfur orbital to the  $3 a_2$  orbital. The HMO calculation predicts this band at 38,440 cm<sup>-1</sup> ( $1.24 \beta$ ), whereas the OMO calculation predicts it at 41,983 cm<sup>-1</sup>. Thus the assignment is reasonable and is further supported by the observation that the band moves to higher energy in the more polar CH<sub>3</sub>OH solvent. Curiously, there appears to be no splitting of this band as observed in planar  $\alpha$ -diketones and  $\alpha$ -dicarboxylic acid derivatives [6, 9]. Either the geometry of (CH<sub>3</sub>)<sub>2</sub>mnt is such that the nonbonding orbitals on sulfur do not interact, or

that the rather polar solvents [5] used in this study favor a conformation that separates the nonbonding orbitals. (This problem is presently under investigation.) The  $n \rightarrow \pi^*$ -transition from the nitrogen atom is probably of too high an energy to be observed.

In summary, both calculations account reasonably well for the spectrum of the molecule. The highest-filled level is approximately nonbonding with respect to carbon in the HMO scheme and slightly antibonding in that respect in the OMO calculation. The calculations agree that the highest filled level is slightly antibonding with respect to sulfur and nitrogen. The population analysis of the occupied levels for the atoms of  $(\text{CH}_3)_2$  mnt is given in Tab. 3. It is noteworthy that both calculations lead to very similar orbital populations for this molecule.

Table 3. *Population Analysis of Bis-(Methylmercapto)maleonitrile*

Atom	HMO	OMO
S (7) = S (8)	1.85	1.76
C (1) = C (2)	1.10	1.10
N (5) = N (6)	1.19	1.30
C (3) = C (4)	.86	.84

*Bis-(Methylmercapto)fumarionitrile* [ $(\text{CH}_3)_2$  fnt]. The molecular orbitals of this molecule of  $C_{2h}$  symmetry are of the same form as those of  $(\text{CH}_3)_2$  mnt. The symmetry properties of the orbitals, of course, are different. They are presented

Table 4. *Energies and Symmetry Properties of the  $\pi$ -Molecular Orbitals of Bis-(Methylmercapto) fumarionitrile*

MO	HMO energy	OMO energy ( $\text{cm}^{-1}$ )
1 $a_u$	$\alpha + 2.37 \beta$	- 135,857
1 $b_g$	$\alpha + 2.22 \beta$	- 132,764
2 $a_u$	$\alpha + 1.25 \beta$	- 120,375
2 $b_g$	$\alpha + .62 \beta$	- 104,487
3 $a_u$	$\alpha + .06 \beta$	- 79,142
3 $b_g$	$\alpha - .84 \beta$	- 51,417
4 $a_u$	$\alpha - 1.68 \beta$	57,118
4 $b_g$	$\alpha - 2.00 \beta$	127,991

in Tab. 4. The highest filled level is 3  $a_u$ . The pattern of absorption of  $(\text{CH}_3)_2$  fnt in methanol (Tab. 1) is very similar to that of  $(\text{CH}_3)_2$  mnt and the transitions are assigned accordingly:

29,350 $\text{cm}^{-1}$	3 $a_u \rightarrow 3 b_g$
36,630 $\text{cm}^{-1}$	$n(S) \rightarrow 3 b_g$
46,840 $\text{cm}^{-1}$	2 $b_g \rightarrow 3 b_g$ .

The population analysis of this molecule is the same as that for  $(\text{CH}_3)_2$  mnt (see Tab. 3).

*Acrylonitrile, maleonitrile, fumarionitrile, and tetracyanoethylene.* Due to their structural similarities we shall discuss as a group the simple molecules containing only nitrile functional groups.

The energy level schemes calculated by both methods are given in Tab. 5. All the molecules have their highest filled levels bonding with respect to C and N. The calculated separation of the highest filled and lowest empty  $\pi$ -levels decreases as

the number of nitrile groups attached to the ethylene framework increases. Thus, we have the order acrylonitrile > maleonitrile = fumaronitrile > tetracyanoethylene (TCNE) for the spectroscopically important separations.

Population analysis are given in Tab. 6. All the molecules studied show a build-up of charge on the nitrogen atoms at the expense of the adjacent carbon atoms.

Table 5. *Energies and Symmetry Properties of the  $\pi$ -Molecular Orbitals*

Tetracyanoethylene			
MO	HMO energy	OMO energy (cm <sup>-1</sup> )	
1 $b_{3u}$	$\alpha + 2.52 \beta$	- 137,164	
1 $b_{1g}$	$\alpha + 2.30 \beta$	- 133,428	
1 $a_u$ , 1 $b_{2g}$	$\alpha + 2.12 \beta$	- 130,486	
2 $b_{3u}$	$\alpha + .88 \beta$	- 111,481	
2 $b_{1g}$	$\alpha - .49 \beta$	- 75,575	
2 $b_{2g}$ , 2 $a_u$	$\alpha - 1.52 \beta$	- 23,097	
3 $b_{3u}$	$\alpha - 1.80 \beta$	122,046	
3 $b_{1g}$	$\alpha - 2.21 \beta$	181,255	

Maleonitrile MO	HMO energy	OMO energy (cm <sup>-1</sup> )	Fumaronitrile MO
1 $b_1$	$\alpha + 2.34 \beta$	- 134,128	1 $a_u$
1 $a_2$	$\alpha + 2.21 \beta$	- 131,740	1 $b_g$
2 $b_1$	$\alpha + 0.93 \beta$	- 112,066	2 $a_u$
2 $a_2$	$\alpha - 0.66 \beta$	- 67,355	2 $b_g$
3 $b_1$	$\alpha - 1.67 \beta$	- 2,951	3 $a_u$
3 $a_2$	$\alpha - 1.95 \beta$	7,600	3 $b_g$

Acrylonitrile		
MO	HMO energy	OMO energy (cm <sup>-1</sup> )
1	$\alpha + 2.28 \beta$	- 132,907
2	$\alpha + 0.96 \beta$	- 112,902
3	$\alpha - 0.81 \beta$	- 55,167
4	$\alpha - 1.83 \beta$	40,105

$\pi \rightarrow \pi^*$ -bands. All the nitrile-containing molecules studied show one band due to an allowed  $\pi \rightarrow \pi^*$  transition. Tetracyanoethylene exhibits this transition at 40,520 cm<sup>-1</sup> (MeOH,  $\epsilon = 11,800$ ). The OMO calculation predicts the band at ca. 35,906 cm<sup>-1</sup> while the HMO calculation gives it at 42,470 cm<sup>-1</sup> ( $\Delta E = 1.37 \beta$ ). According to both calculations the band is 2  $b_{3u} \rightarrow 2 b_{1g}$  ( $1A_g \rightarrow 1B_{2u}$ ), which is an allowed transition.

According to the approximations employed in this work, fumaronitrile and maleonitrile have the same energy level scheme. In each case the allowed  $\pi \rightarrow \pi^*$  transition is calculated at 49,290 cm<sup>-1</sup> ( $1.59 \beta$ ) by the HMO method and at

44,711  $\text{cm}^{-1}$  by the OMO method. An intense band is observed in each molecule at approximately 45,450  $\text{cm}^{-1}$  ( $\epsilon = 14,480$  for maleonitrile;  $\epsilon = 15,880$  for fumaronitrile) in EtOH in good agreement with the calculations. The detailed assignment for fumaronitrile is  $2 a_u \rightarrow 2 b_g$  ( ${}^1A_g \rightarrow {}^1B_u$ ) while for maleonitrile the assignment is  $2 b_1 \rightarrow 2 a_2$  ( ${}^1A_1 \rightarrow {}^1B_2$ ).

In acrylonitrile an intense band ( $\epsilon = 10,000$ ) is observed at ca. 51,800  $\text{cm}^{-1}$ . The HMO calculation gives this band at 54,870  $\text{cm}^{-1}$  ( $\Delta E = 1.77 \beta$ ) while the OMO calculation predicts it at 57,735  $\text{cm}^{-1}$ .

None of the  $\pi \rightarrow \pi^*$  transitions is associated with any large transfer of charge. In other words, the transitions are between highly delocalized  $\pi$ -orbitals. This

Table 6. *Population Analysis of the Occupied  $\pi$ -Levels*

Atom	HMO	OMO
Tetracyanoethylene		
C(3) = C(4)	.96	.92
N(8) = N(10) = N(1) = N(6)	1.18	1.24
C(2) = C(5) = C(7) = C(9)	.86	.80
Acrylonitrile		
C(1)	.96	.92
C(2)	1.02	1.02
C(3)	.85	.80
N(4)	1.18	1.26
Fumaronitrile (Maleonitrile)		
C(2) = C(5)	.92	.80
C(3) = C(4)	.96	.95
N(1) = N(6)	1.12	1.25

interpretation is consistent with the fact that the  $\pi \rightarrow \pi^*$ -bands are essentially unaffected by changing the polarity of the solvent employed. This is nicely illustrated for acrylonitrile in Tab. 7 and for TCNE in Tab. 1.

*n*  $\rightarrow$   $\pi^*$  bands. Weak bands attributed to perpendicular transitions involving the excitation of a nonbonding electron from the nitrogen of a nitrile group to the lowest  $\pi^*$  level (*n*  $\rightarrow$   $\pi^*$ ) are observed in the spectra of acrylonitrile and tetracyanoethylene. To our knowledge, similar weak bands have not been observed in the spectra of fumaronitrile and maleonitrile.

In addition to one strong band ( $\pi \rightarrow \pi^*$ ) at 40,733  $\text{cm}^{-1}$  in EtOH, TCNE also displays a shoulder at ca. 34,000  $\text{cm}^{-1}$ . This shoulder is assigned as the *n*  $\rightarrow$   $\pi^*$  ( $2 b_{1g}$ ) transition predicted at 33,700  $\text{cm}^{-1}$  ( $1.09 \beta$ ) by the HMO method and at 30,825  $\text{cm}^{-1}$  by OMO calculation. In the more polar  $\text{CH}_3\text{OH}$  the *n*  $\rightarrow$   $\pi^*$ -transition is probably of higher energy and obscured by the intense 40,520  $\text{cm}^{-1}$  band.

In acrylonitrile, in addition to the allowed band, there is a shoulder at ca. 48,500  $\text{cm}^{-1}$ . This band may be due to the *n*(N)  $\rightarrow$   $\pi^*$  transition. The HMO

calculation predicts this transition at  $1.41 \beta$  ( $43,710 \text{ cm}^{-1}$ ) while the OMO calculation predicts it at  $51,233 \text{ cm}^{-1}$ . Both calculations correctly predict the  $n \rightarrow \pi^*$ -transition at lower energy than the allowed  $\pi \rightarrow \pi^*$ -transition.

Although the presence of vibrational structure clouds somewhat the interpretation of the shoulder as due to a separate electronic transition, a limited study in the vapor phase and in three solvents is consistent with our assignment. These results are set out in Tab. 7.

The position of the intense band is relatively insensitive to the solvent; however, the shoulder occurs at higher energy in the more polar solvent acetonitrile than in isoctane. In  $\text{H}_2\text{O}$ , the most polar solvent studied, we hypothesize that the  $n \rightarrow \pi^*$ -band is at high energy and is buried under the intense  $\pi \rightarrow \pi^*$ -band.

Table 7. *Electronic Spectrum of Acrylonitrile*

solvent	$\text{H}_2\text{O}$	Acetonitrile	Isoctane	vapor phase
$\lambda \text{ max } (\pi \rightarrow \pi^*) \text{ \AA}$	1935 <sup>a</sup>	1925	1930 <sup>a</sup>	1930 <sup>a</sup>
$\lambda \text{ (shoulder) \AA}$	—	2025	2060	2060

<sup>a</sup> Exact location of peaks is uncertain.

### Summary and Conclusions

Comparing the results of the two types of calculations, we find that, except for the fumaronitrile case, the HMO method gives better agreement with the spectra than the OMO method. However, this is simply due to the fact that all the HMO molecular parameters were varied to obtain the best fit with the spectra. The OMO results are all in reasonable agreement with the spectra and, from a theoretical point of view, much more satisfying since in this method there is only one adjustable parameter (the  $F$ -factor). The  $F$ -factor of 2.3 was not changed from molecule to molecule. Significantly, for each molecule investigated both calculations gave the same results in two important respects:

1. the energy ordering of the molecular orbitals;
2. the assignments of the spectral bands.

In addition, the eigenvectors and resulting population analysis of the molecules are similar in both sets of calculations.

### Comparison of HMO and OMO Parameters

It was deemed desirable to compare the empirical HMO molecular parameters with the semi-empirical OMO parameters. In order to do this, the OMO parameters were converted to HMO form.

#### *a) Coulomb integrals*

The standard HMO form for the coulomb integral is  $\alpha_Y = \alpha_X + c\beta_{XX}$  where  $\alpha_X$  refers to a standard  $\alpha$ , usually  $\alpha_C$ , and  $\beta_{XX}$  refers to a standard  $\beta$  (ethylene  $\beta_{C-C} = -31,000 \text{ cm}^{-1}$ ) and  $c$  is a number.

To convert the OMO parameters to HMO form we made use of the average carbon VOIP; thus  $\alpha = -85,000 \text{ cm}^{-1}$ . Therefore, our  $\alpha_N (-106,400) = \alpha + .7 \beta$  while  $\alpha_S (-93,400) = \alpha + .3 \beta$ .

## b) Resonance integrals

The standard HMO form for resonance integrals is  $\beta_{AB} = k\beta_{XX}$  where  $\beta_{XX}$  is a standard  $\beta$  and  $k$  is a number. Since  $\beta_{AB}$  is dependent on  $S_{AB}$  (and thus on bond length), it varies from molecule to molecule. In Tab. 8 the various values of  $\beta_{AB}$  are tabulated. First the  $\beta$ -values are given in terms of the ethylene  $\beta$  ( $\beta'$ ), and then, since the ratios of the  $\beta$ 's are critical in HMO calculations, they are expressed in terms of  $\beta_{CC}$  ( $\beta$ ) for the particular molecule involved. In Tab. 9 the HMO and

Table 8

mnt		C - C - CN	
$\beta_{C-S}$	$= -48,447 = 1.56 \beta' = .68 \beta$	$\beta_{C-N}$	$= -79,684 = 2.58 \beta' = 1.19 \beta$
$\beta_{C-N}$	$= -82,958 = 2.68 \beta' = 1.16 \beta$	$\beta_{C-CN}$	$= -58,018 = 1.87 \beta' = .87 \beta$
$\beta_{C-CN}$	$= -59,557 = 1.92 \beta' = .84 \beta$	$\beta_{C-C}$	$= -66,780 = 2.15 \beta' = \beta$
$\beta_{C-C}$	$= -71,081 = 2.29 \beta' = \beta$		

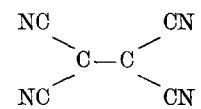
NC - C - C - CN			
$\beta_{C-N}$	$= -79,684 = 2.57 \beta' = 1.19 \beta$	$\beta_{C-N}$	$= -80,076 = 2.58 \beta' = 1.16 \beta$
$\beta_{C-CN}$	$= -59,557 = 1.92 \beta' = .89 \beta$	$\beta_{C-CN}$	$= -58,945 = 1.90 \beta' = .85 \beta$
$\beta_{C-C}$	$= -67,096 = 2.16 \beta' = \beta$	$\beta_{C-C}$	$= -69,602 = 2.25 \beta' = \beta$

Table 9

	HMO	OMO <sup>a</sup>
$\alpha_N$	$\alpha + .6 \beta'$	$\alpha + .7 \beta'$
$\alpha_S$	$\alpha + .4 \beta'$	$\alpha + .3 \beta'$
$\alpha_C$	$\alpha$	$\alpha$

		mnt	Fumaronitrile	Acrylonitrile	TCNE
$\beta_{C-C}$	$\beta'$	$\beta^a$	$\beta^a$	$\beta^a$	$\beta^a$
$\beta_{C-CN}$	$.8 \beta'$	$.84 \beta$	$.89 \beta$	$.87 \beta$	$.85 \beta$
$\beta_{C-N}$	$1.8 \beta'$	$1.16 \beta$	$1.19 \beta$	$1.19 \beta$	$1.16 \beta$
$\beta_{C-S}$	$.6 \beta'$	$.68 \beta$	-	-	-

<sup>a</sup>  $\beta = \beta_{AB}$  in molecule in question; (actual values in  $\text{cm}^{-1}$ ) of  $\beta$  in the various molecules; mnt = - 71,082; fumaronitrile = - 67,046; acrylonitrile = - 66,780; TCNE = - 69,602.

OMO parameters are compared. The parameters are reasonably consistent from molecule to molecule in the OMO series. The parameters in this series are qualitatively very similar to the HMO parameters.

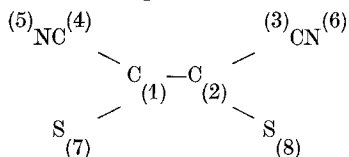
## Experimental

Samples of  $(\text{CH}_3)_2$  mnt and  $(\text{CH}_3)_2$  fnt were prepared according to previously published methods [10]. Reagent grade tetracyanoethylene and spectral grade acrylonitrile were used. All spectra were measured on a Cary 14 Spectrophotometer.



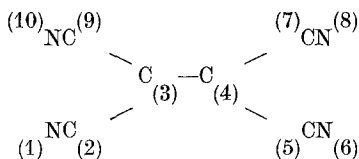
## Appendix

Eigenvectors



## 1. Bis(Methylmercapto)maleonitrile

	1	2	3	4	5	6	7	8	
OMO	.30	.30	.32	.32	.34	.34	.11	.11	1 $b_1$
HMO	.30	.30	.44	.44	.45	.45	.09	.09	
OMO	-.11	.11	.36	-.36	-.45	.45	-.05	.05	1 $a_2$
HMO	-.12	.12	.44	-.44	-.45	.45	-.05	.05	
OMO	-.39	-.39	.14	.14	.37	.37	-.29	-.29	2 $b_1$
HMO	-.51	-.51	.11	.11	.30	.30	-.36	-.36	
OMO	-.27	.27	.01	-.01	-.17	.17	-.59	.59	2 $a_2$
HMO	-.24	.24	.01	-.01	-.10	.10	-.65	.65	
OMO	-.30	-.30	-.11	-.11	.22	.22	.63	.63	3 $b_1$
HMO	-.34	-.34	-.04	-.04	.15	.15	.59	.59	
OMO	.38	-.38	-.42	.42	-.49	.49	-.33	.33	3 $a_2$
HMO	.49	-.49	-.28	.28	-.34	.34	-.23	.23	
OMO	.31	.31	-.71	-.71	.54	.54	-.16	-.16	4 $b_1$
HMO	.17	.17	-.51	-.51	.42	.42	-.05	-.05	
OMO	.90	-.90	.63	-.63	.35	-.35	-.32	.32	3 $a_2$
HMO	.42	-.42	.45	-.45	.31	-.31	-.11	.11	

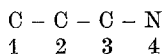


## 2. Tetracyanoethylene

	1	2	3	4	5	6	7	8	9	10	
OMO	.24	.24	.29	.29	.24	.24	.24	.24	.24	.24	1 $b_{3u}$
HMO	.30	.32	.34	.34	.32	.30	.32	.30	.32	.30	
OMO	-.31	-.26	-.14	.14	.26	.31	.26	.31	-.26	-.31	1 $b_{1g}$
HMO	-.35	-.33	-.16	.16	.33	.35	.33	.35	-.33	-.35	
OMO	.35	.26	0	0	-.26	-.35	.26	.35	-.26	-.35	1 $a_u$
HMO	.54	.45	0	0	-.45	-.45	.45	.54	-.45	-.54	
OMO	.35	.26	0	0	.26	.35	-.26	-.35	-.26	-.35	1 $b_{2g}$
HMO	.54	.45	0	0	.45	.54	-.45	-.54	-.45	-.54	

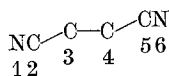
## 2. Tetracyanoethylene (Fortsetzung)

	1	2	3	4	5	6	7	8	9	10	
OMO	.32	.04	-.46	-.46	.04	.32	.04	.32	.04	.32	2 $b_{3u}$
HMO	.28	.04	-.58	-.58	.04	.28	.04	.28	.04	.28	
OMO	-.36	.21	.47	-.47	-.21	.36	-.21	.36	.21	-.36	2 $b_{1g}$
HMO	-.28	.17	.53	-.53	-.17	.28	-.17	.28	.17	-.28	
OMO	-.41	.47	0	0	-.47	.41	.47	-.41	-.47	.41	2 $a_u$
HMO	-.46	.54	0	0	-.54	.46	.54	-.46	-.54	.46	
OMO	-.41	.47	0	0	.47	-.41	-.47	.41	-.47	.41	2 $b_{2g}$
HMO	-.46	.54	0	0	.54	-.46	-.54	.46	-.54	.46	
OMO	.37	-.53	.38	.38	-.53	.37	-.53	.37	-.53	.37	3 $b_{3u}$
HMO	.29	-.38	.22	.22	-.38	.29	-.38	.29	-.38	.29	
OMO	.29	-.56	.95	-.95	.56	-.29	.56	-.29	-.56	.29	3 $b_{1g}$
HMO	.21	-.33	.44	-.44	.33	-.21	.33	-.21	-.33	.21	



## 3. Acrylonitrile

	1	2	3	4	
OMO	.12	.26	.50	.60	1
HMO	.12	.28	.65	.70	
OMO	-.58	-.55	.07	.40	2
HMO	-.68	-.65	.07	.33	
OMO	.72	-.46	.49	.57	3
HMO	.68	-.55	.30	.38	
OMO	-.53	.84	-.89	.58	4
HMO	-.24	.43	-.70	.52	



## 4. Fumaronitrile

	1	2	3	4	5	6	
OMO	.34	.35	.25	.25	.35	.34	1 $a_u$
HMO	.47	.45	.27	.27	.45	.47	
OMO	-.46	-.37	-.11	.11	.37	.46	1 $b_g$
HMO	-.52	-.47	-.12	.12	.47	.52	
OMO	.38	.06	-.52	-.52	.06	.38	2 $a_u$
HMO	.31	.06	-.63	-.63	.06	.31	
OMO	-.48	.34	.51	-.51	-.34	.48	2 $b_g$
HMO	-.34	.24	.57	-.57	-.24	.34	
OMO	.54	-.71	.28	.28	-.71	.54	3 $a_u$
HMO	.43	-.54	.16	.16	-.54	.43	
OMO	-.39	.66	-.79	.79	-.66	.39	3 $b_g$
HMO	-.34	.48	-.40	.40	-.48	.34	

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