

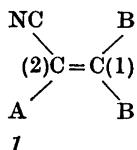
## Photoelectron Spectra of Some Simple Push-pull Ethylenes

D. BETTERIDGE,<sup>a</sup> L. HENRIKSEN,<sup>b</sup> J. SANDSTRÖM,<sup>c</sup> I. WENNERBECK<sup>c</sup> and M. A. WILLIAMS<sup>a</sup><sup>a</sup>Department of Chemistry, University College of Swansea, Swansea SA2 8PP (Wales),<sup>b</sup>Chemical Laboratory II, The H.C. Ørsted Institute, DK-2100 Copenhagen, Denmark and <sup>c</sup>Division of Organic Chemistry, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund 7, Sweden

The photoelectron spectra of a number of push-pull ethylenes with alkylthio, alkylseleno, and dialkylamino groups as electron donors and cyano groups as electron acceptors have been studied together with those of some simpler reference compounds containing either the donor or the acceptor groups. Band assignments have been made utilizing qualitative orbital interaction schemes, symmetry arguments, and CNDO/2 calculations. The band with lowest IP in all cases is ascribed to a delocalized  $\pi$ -orbital, and the second band in the molecules with donor groups to the antisymmetric combination of the donor atom  $p_z$  orbitals. The effect of ring size when the donor atoms are included in cyclic systems is also discussed.

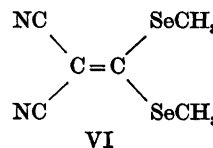
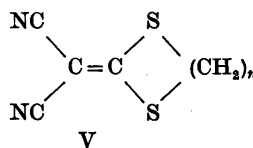
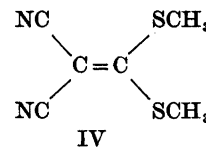
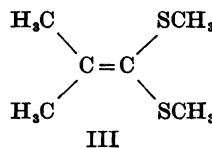
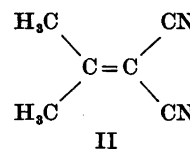
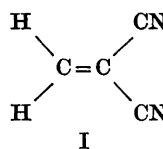
The powerful stabilizing influence of donor and acceptor groups interacting across a carbon-pi-framework, which has been termed the push-pull effect, was elegantly demonstrated when Gompper and Seybold<sup>1</sup> succeeded in preparing a stable push-pull substituted cyclobutadiene.

Doubly push-pull substituted ethylenes in which at least one acceptor group is a cyano function and the donor groups contain sulfur, selenium or nitrogen atoms (*I*) are convenient models for studies of the push-pull effect. These compounds are readily accessible, and the substituents are well suited for the push-pull interaction.

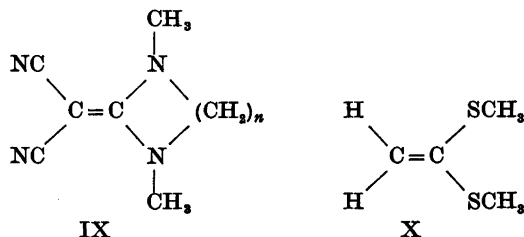
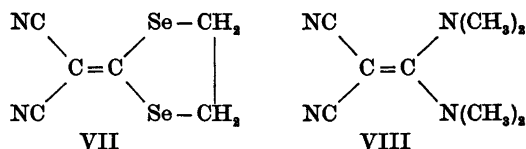
A = CN, CO<sub>2</sub>R, CONR<sub>2</sub>, CORB = SR, SeR, NR<sub>2</sub>

dipole moments<sup>5</sup>) and dynamic physical properties (activation barriers for internal rotations).<sup>6-8</sup> Also the chemical properties reflect this interaction. Thus the central double bond undergoes neither oxidation nor reduction under mild conditions.<sup>9</sup> Nucleophiles attack at C(1)<sup>10</sup> and electrophiles at C(2)<sup>11</sup> and in both cases the reaction course leads to substitution rather than to addition showing the resistance toward disruption of the push-pull system.

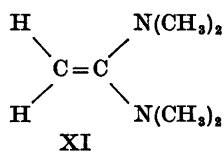
In order to obtain further information about the effect of push-pull substituents on the electronic structure, and especially on basis orbital participation in the molecular orbitals, photoelectron spectra (PES) of a number of simple push-pull ethylenes have been studied (I–IX).

a,  $n = 3$ b,  $n = 2$ c,  $n = 1$ 

The push-pull interaction in *I* has been evidenced by several previous investigations of their static (UV-<sup>2</sup> and IR-spectra<sup>3,4</sup> and



a,  $n = 2$   
b,  $n = 3$



The compounds chosen are a series of 1,1-dicyanoethylenes with sulfur (IV and V), selenium (VI and VII) or nitrogen (VIII and IX) atoms as electron donors. For comparison, two 1,1-dicyanoethylenes (I and II) and one 1,1-bismethylthioethylene (III) have also been studied. Bock *et al.*<sup>13</sup> have recently described and interpreted the PES of some ethylenes with alkoxy, alkylthio, and dimethylamino substituents, and these form a suitable series of reference compounds for our study.

## EXPERIMENTAL

**Preparative part.** All compounds have been prepared by literature methods: I,<sup>13</sup> II,<sup>14</sup> III,<sup>15</sup> IV,<sup>9</sup> Va,<sup>9</sup> Vb,<sup>9</sup> Vc,<sup>16</sup> VI,<sup>17</sup> VII,<sup>17</sup> VIII,<sup>18</sup> IXa<sup>18</sup> and IXb.<sup>5</sup>

**Instrument part.** The spectra were obtained with a photoelectron spectrometer with a magnetic electron-energy analyzer, which has been described elsewhere.<sup>19,20</sup> The samples were heated to give a pressure of 1.3 Pa, and the temperature (°C) of the heating flange at this point for the different samples was: I:53; II:19; III:19; IV:90; Va:100; Vb:160; Vc:102; VI:65; VII:101; VIII:131; IXa:167; IXb:100.

Calibration was carried out with the  $P_{3/2}$  and  $P_{1/2}$  peaks of argon and xenon. The experimental values quoted relate to vertical ionization potentials and have an accuracy of  $\pm 0.05$

eV for well defined peaks and  $\pm 0.1$  eV for broad bands.

**CNDO/2 calculations.** These have been performed without  $d$ -orbitals for sulfur, using a revised version<sup>21</sup> of the original program.<sup>22</sup> No calculations have been performed on the selenium compounds. The geometries of all systems treated except those of Vb and Vc are given in Ref. 5. The geometry of the dithiolane ring in Vb is assumed to be the same as in ethylene trithiocarbonate,<sup>23</sup> where it is somewhat twisted, and the geometry of the dithietane ring in Vc is taken from the structure of an adduct from 3-diazobutanone and carbon disulfide.<sup>24</sup> The  $(NC)_2C=CX_2$  part of the molecules are placed in the  $XY$  plane.

## RESULTS AND DISCUSSION

The schematic molecular orbital diagram for the combination of the  $\pi$  orbitals of a 1,1-dicyanoethylene moiety and the  $p_x$  orbitals of the donor atoms (Fig. 1) is used as a basis for the following discussion.

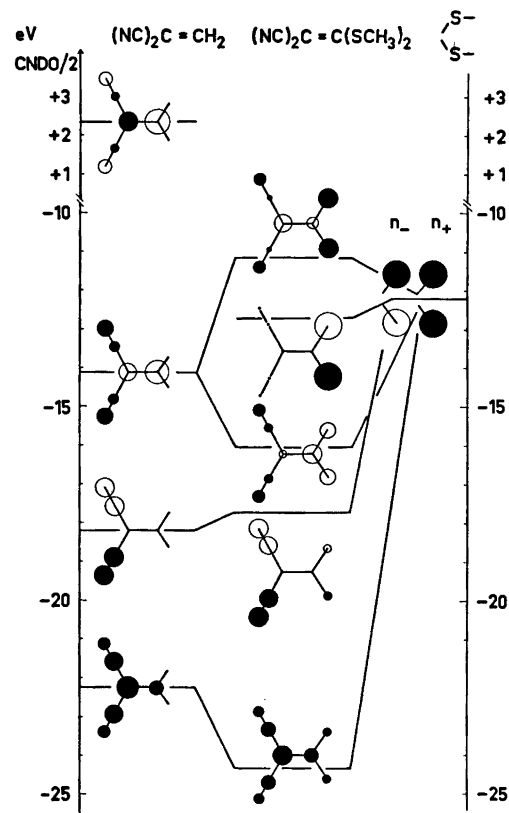


Fig. 1. Molecular orbital diagram for the  $\pi$  orbitals of  $(NC)_2C=CX_2$ .

Compounds I–III have been studied as reference systems. The PES of *cis*- and *trans*-1,2-dicyanoethylene have been analyzed by Bock and Stafast.<sup>25</sup> Both compounds show a first peak typical of ionization from a  $\pi$ -orbital at 11.15 eV, *i.e.* with somewhat higher IP than the  $\pi$ -orbital in ethylene (10.51 eV<sup>26</sup>). The coupling of the C $\equiv$ N and C=C  $\pi$ -orbitals alone should raise the highest occupied MO (HOMO), but charge displacement to the cyano groups and interaction with the LFMO of the cyano groups will lower the C=C  $\pi$ -orbital, and the net result is a lowering of the HOMO. The same effect is observed in I, though the coupling here is less efficient since it results in cross-conjugation. Its PES displays a first peak at 11.29 eV with a short progression of spacings of ca 1400 cm<sup>-1</sup>, indicating ionization from a  $\pi$ -orbital mainly localized in the C=C bond. According to the calculations, this orbital is an antibonding combination of the bonding C=C  $\pi$ -orbital and the symmetric C $\equiv$ N  $p_x$  orbital combination with the largest contribution from the C=C bond. The following peak, centered at 13.5 eV, is quite broad and probably contains several ionizations. After the present work was concluded, the PES of I was published<sup>27</sup> with essentially the same interpreta-

tion as the one given above.

The PES of II is rather similar to that of I, only with the first peak appearing at 10.21 eV. This difference can be ascribed to the inductive and hyperconjugative effect of the methyl groups, in agreement with calculations.

1,1-Bismethylthio-2-methylpropene (III) displays four well resolved peaks at 8.12, 8.77 (sharp), 9.84, and 10.66 eV, followed by a group of strongly overlapping bands. The spectrum is rather similar to that of 1,1-bismethylthioethylene<sup>12</sup> (X), and the interpretation of the first two peaks is the same as that given by Bock *et al.*<sup>12</sup> The first peak is ascribed to ionization from a  $\pi$ -orbital, which is an antibonding combination of the C=C  $\pi$ -orbital and the symmetric combination of the sulfur  $p_x$  orbitals, the second peak to the asymmetric combination of the sulfur  $p_x$  orbitals, and the fourth peak to the bonding combination of these orbitals. The first of these orbitals is referred to in the following as  $n_+$ , the second as  $n_-$ , and the third as  $n_+$ . The difference of 1.89 eV between  $n_-$  and  $n_+$  is then a measure of the interaction between the sulfur  $p_x$  orbitals and the C=C  $\pi$ -orbitals. The different effect of methyl substitution in the dicyanoethylenes and bismethylthioethylenes is worth noticing.

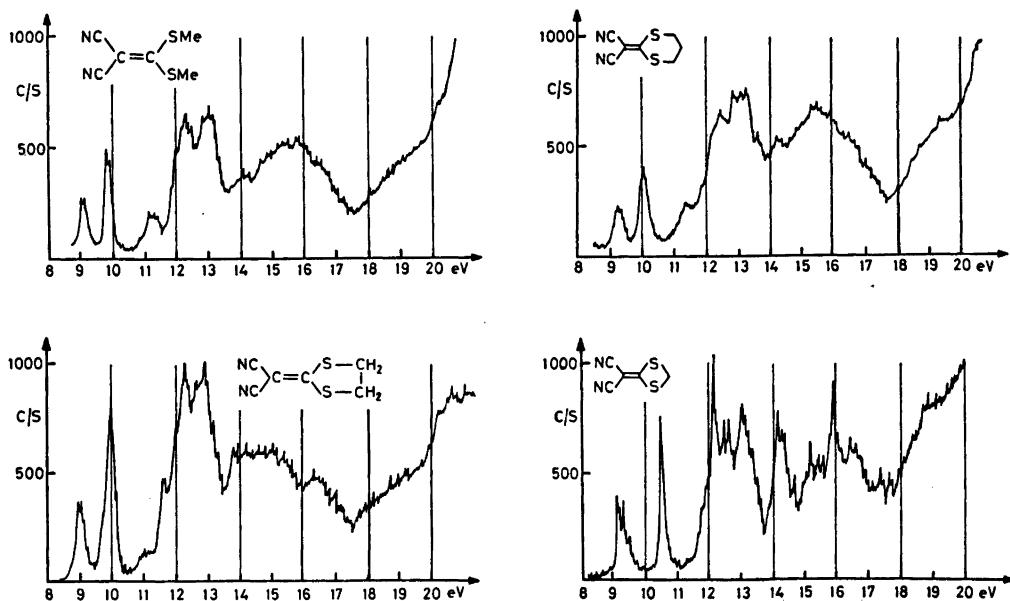


Fig. 2. UV photoelectron spectra of IV, Va, Vb, and Vc.

In the first set of compounds, two methyl groups lower the IP of the highest  $\pi$ -orbital with *ca.* 1.1 eV, whereas in the methylthio compounds the two first bands are virtually unaffected by methyl substitution. This is in agreement with simple perturbation arguments based on the energy differences between the interacting groups.<sup>28</sup>

The PES of 1,1-bismethylthio-2,2-dicyanoethylene (IV) displays three resolved bands at 9.16, 9.89 (sharp), and 10.20 eV followed by a series of overlapping bands (Fig. 2). Symmetry arguments, the shape of the band, and the calculations all agree in assigning the first band to ionization from an antibonding combination of the  $\pi_1$  orbital in the  $S_2C=C$  part and the symmetric combination of the  $p_z$  orbitals in the CN groups (Fig. 1), and the second band to the  $n_-$  orbital. The third band is according to the calculations ascribed to a  $\sigma$ -orbital with strong contribution from the sulfur atoms. The introduction of sulfur lowers the  $\pi_1$  IP in IV relative to that in II by 1.05 eV.

The six-membered cyclic analog Va has a spectrum rather similar to that of IV, the main difference being a shift of the second band by 0.14 eV to higher IP. The five-membered analog Vb has a higher IP for the third band (11.55 eV) and shows a barely resolved vibrational structure in the first band with a spacing of *ca.* 1200  $cm^{-1}$ , which is reasonable for ionization from an orbital with considerable C=C bond character. The IR spectrum of Vb has a strong band at 1480  $cm^{-1}$ , which is assigned to a vibration dominated by C=C stretching.<sup>3</sup>

The first band in the spectrum of the compound with the four-membered ring, Vc, shows

a clear vibrational structure with a spacing of 1250  $cm^{-1}$ . The corresponding IR band appears at 1505  $cm^{-1}$  and has more C=C stretching character than the analogous bands in Vb.<sup>3</sup> The lack of fine structure in the first band in IV and Va may be due to flexibility and the existence of several conformers. It has been shown by dipole moment measurements that IV exists as an equilibrium mixture of the *Z,Z*, the *E,Z*, and possibly also the *E,E* conformations.<sup>5</sup>

The second band of Vc is sharper than in any of the analogous compounds, indicating ionization from an orbital with insignificant bonding character. Its IP is also higher (10.50 eV) than in IV, Va and Vb (9.89–10.03 eV). In the latter compounds the  $n_-$  orbital can interact in an antibonding fashion with the antisymmetric combination of the  $2p_z$  orbitals on the neighbouring carbon atoms, and to some extent also with combinations of the hydrogen  $1s$  orbitals of suitable symmetry, which raises the energy of the  $n_-$  orbitals in these compounds. Such interactions are demonstrated by the CNDO/2 calculations. In an alternative but equivalent description  $n_-$  interacts with combinations of the C–H bond orbitals of suitable symmetry. In Vc the atoms of the  $CH_2$  group are in the nodal plane of the  $n_-$  orbital and no interaction is possible, which probably accounts for the high IP.

The seleno compounds VI and VII have spectra rather similar to those of the sulfur analogs (Fig. 3), but with lower IP:s of the three first bands, which are assigned similarly, *i.e.*  $\pi_1$ ,  $n_-$ , and  $\sigma_{C-Se}$ , respectively. This reflects the difference in IP of the sulfur and selenium atoms (IP for  $S(^3P_2)$ : 10.35 eV, for  $Se(^3P_2)$ : 9.75 eV).<sup>29</sup> The first band is shifted 0.31 eV from IV to

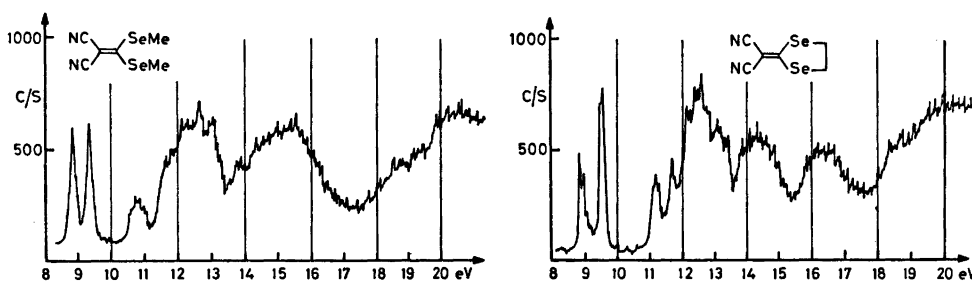


Fig. 3. UV photoelectron spectra of VI and VII.

VI, and 0.06 eV from Vb to VII. For the second band the corresponding shifts are 0.50 and 0.40 eV and the third band 0.47 and 0.40 eV, respectively. The larger shifts for the second and third band are in agreement with ionization from orbitals with dominating S(Se) character. In Vb and VII non-planarity of the ring causes some mixing of the S(Se) outer-shell  $p_z$  orbitals with other orbitals. This diminishes the proportion of S(Se) basis orbitals in the first two molecular orbitals relative to the non-cyclic analogs IV and VI, which probably accounts for the smaller effect of replacement of sulfur by selenium in the cyclic compounds. It may also explain the differences in intensities of the  $\pi_1$  bands in VI and VII. The areas of the first two bands in VI are almost equal, suggesting a considerable mixing of the Se  $p_z$  and C=C  $\pi$  orbitals.

In the spectra of the 1,1-dicyano-2,2-diamino compounds VIII, IXa and IXb (Fig. 4), two bands appear at low IP, followed by a system of poorly resolved bands above 11 eV. In VIII and also in IXb the second band is sharper than the first, but both bands are considerably broader than the first two bands in the sulfur and selenium analogs.

The assignment is analogous to the one given for the compounds IV to VII, in agreement with calculations and also with the analysis of the PES of 1,1-bisdimethylaminoethylene (XI) given by Bock *et al.*<sup>12</sup> Also in this case introduction of the cyano groups causes a lowering of the two highest orbitals (Table 1). This effect, however, is not brought out by the calculations, which may be ascribed to a general tendency of the CNDO/2 method to underestimate the electron-withdrawing effect of cyano groups.<sup>30,31</sup> The experimental IP:s for the first band are 7.5 eV for XI and 8.21 for VIII, and the calculated values are 10.49 *versus* 10.14 eV. For the second band, at 8.2 eV for XI and at 9.17 eV for VIII, the calculated values of 11.77 and 12.14 eV fall in the right order, but the difference is strongly underestimated.

The conformations of the diamines VIII, IXa and IXb are rather different. As discussed before,<sup>5</sup> the dimethylamino groups in VIII, and also in XI, cannot be in the molecular plane for steric reasons but are probably twisted around the =C-N bond by an angle of *ca.* 20° in the same sense. In IXa and IXb the amino trigonal planes and double bond plane are probably much more coincident, as evidenced

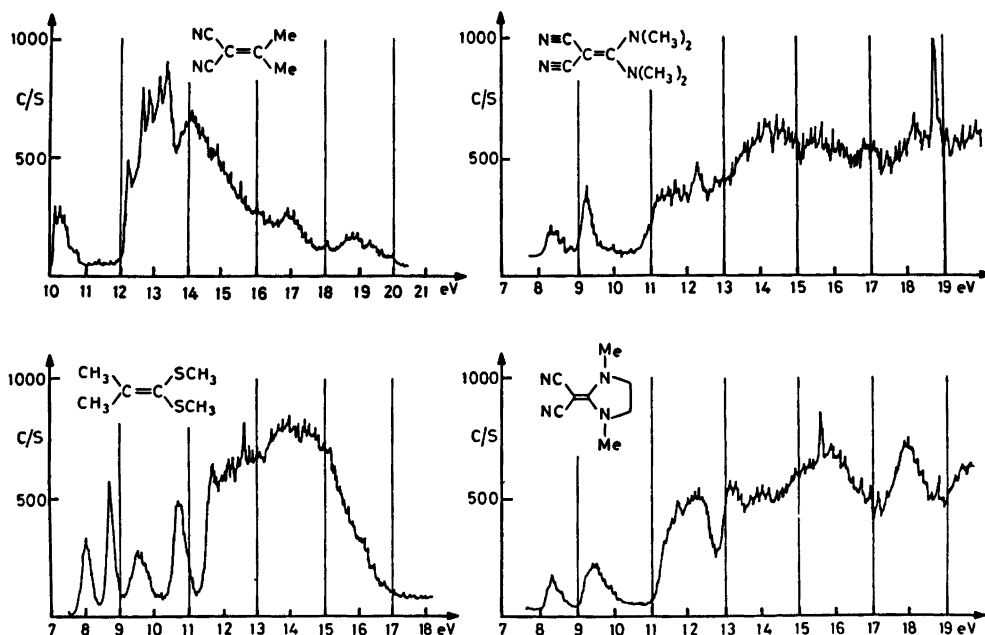


Fig. 4. UV photoelectron spectra of II, III, VIII, and IXa.

Table 1. Experimental and calculated ionization potentials together with band assignments.

Compound	IP (exp) eV	IP (calc) eV	Orbital type
I	11.29 (1400 cm <sup>-1</sup> )	14.10	$\pi (B_2)$
	13.0	15.92	$\sigma (B_2)$
II	10.21 (1100 cm <sup>-1</sup> )	12.52	$\pi (B_2)$
	12.23	15.16	$\sigma (B_2)$
III	8.12	10.58	$\pi (B_2)$
	8.74	11.98	$n_- (A_2)$
	9.54	11.98	$\sigma$
	10.66	13.08	$n_+$
IV	9.16	11.15	$\pi (B_2)$
	9.89	12.70	$n_- (A_2)$
	11.20	12.71	$\sigma$
	12.02	13.30	$\sigma$
Va	9.18	11.38	$\pi (B_2)$
	10.03	11.83	$n_- (A_2)$
	11.39	12.34	$\sigma$
	12.35	13.27	$\sigma$
Vb	8.88 (1200 cm <sup>-1</sup> )	11.26	$\pi (B_2)$
	9.94	12.66	$n_- (A_2)$
	11.55	12.76	$\sigma$
	12.16	13.97	$\sigma$
Vc	9.08 (1250 cm <sup>-1</sup> )	11.51	$\pi (B_2)$
	10.50	12.99	$n_- (A_2)$
	11.92	11.51	$\sigma$
	12.1	14.58	$\sigma$
VI	8.85		$\pi (B_2)$
	9.39		$n_- (A_2)$
	10.73		
	11.59		
VII	8.82		$\pi (B_2)$
	9.54		$n_- (A_2)$
	11.15		
	11.63		
VIII	8.21	10.15	$\pi (B_2)$
	9.17	12.14	$n_- (A_2)$
	11.04	13.90	$\sigma$
	11.29	14.03	$\sigma$
IXa	8.20	9.81	$\pi (B_2)$
	9.51	12.73	$n_- (A_2)$
	11.47	13.78	$\sigma$
IXb	11.88	14.35	$\sigma$
	8.11	9.73	$\pi (B_2)$
	9.33	12.86	$n_- (A_2)$
	11.26	12.59	$\sigma$
X	8.2 <sup>a</sup>	11.42	$\pi (B_2)$
	8.8 <sup>a</sup>	12.19	$n_- (A_2)$
XI	7.5 <sup>a</sup>	10.49	$\pi (B_2)$
	8.2 <sup>a</sup>	11.77	$n_- (A_2)$
	10.3 <sup>a</sup>	14.51	$\sigma$
	12.5 <sup>a</sup>	14.59	$\sigma$

<sup>a</sup> From Ref. 12.

by an X-ray crystallographic study of an analog of IXa.<sup>23</sup> This conformational difference has only a very small effect on the first band and more important effects on the second band.

The low IP of the latter band in VIII may be due to an antibonding interaction of the  $n_-$  orbital with a combination of N-C(H<sub>3</sub>) bond orbitals of the right symmetry. Such an effect

is also indicated by the calculations.

The general broadness of PES "lone pair" bands in compounds containing nitrogen compared to those of analogous sulfur compounds may be attributed to a generally more bonding character of nitrogen "lone pairs", which reflects the better overlaps between carbon and nitrogen orbitals than between carbon and sulphur orbitals (Figs. 2 and 4).

*Conclusion.* The experimental IP's show that the position of the  $\pi_1$  orbital is greatly affected by substituents. Replacement of H by CN results in an increase in the  $\pi_1$  IP of 1–1.3 eV. For the series  $(\text{CN})_2\text{C}=\text{CX}_2$ , the lowering of the  $\pi_1$  IP relative to X = H ( $\Delta\text{IP}$ ) is:

X	H	CH <sub>3</sub>	SCH <sub>3</sub>	SeCH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>
$\Delta\text{IP}$	0	1.1	2.1	2.4	3.1

The replacement of two methyl groups bonded to X by  $(\text{CH}_2)_n$ , where  $n=1-3$ , has comparatively little effect on the  $\pi_1$  energy. The series given above may be taken as a measure of relative donor efficiency toward a carbon  $\pi$  system. The same order of donor efficiency of CH<sub>3</sub>S and CH<sub>3</sub>Se has previously been suggested on the basis of force constants.<sup>4</sup>

The calculated electron distribution in  $\pi_1$  is in good agreement with reactivity data, which show C<sub>1</sub>, X, and the cyano nitrogen atom to be centra of reactivity towards electrophiles.<sup>11,22</sup>

*Acknowledgements.* Two of the authors (J.S. and I.W.) gratefully acknowledge financial support by the Swedish Natural Sciences Research Council. D.B. and M.A.W. are grateful for support from the Agricultural Research Council and the Science Research Council for grants for instrumentation. M.A.W. is grateful to the T. and E. Williams Trust for a maintenance grant.

## REFERENCES

- Gompper, R. and Seybold, G. *Angew. Chem.* 80 (1968) 804.
- Wennerbeck, I. *Acta Chem. Scand.* 27 (1973) 258.
- Henriksen, L., Nielsen, P. H., Borch, G. and Klæboe, P. *Spectrochim. Acta A* 31 (1975) 373.
- Henriksen, L., Nielsen, P. H., Borch, G. and Klæboe, P. *Spectrochim. Acta A* 31 (1975) 1371.
- Ericsson, E., Marnung, T., Sandström, J. and Wennerbeck, I. *J. Mol. Struct.* 24 (1975) 373.
- Kessler, H. *Chem. Ber.* 103 (1970) 973.
- Wennerbeck, I. and Sandström, J. *Org. Magn. Reson.* 4 (1972) 783.
- Kalinowski, H.-O. and Kessler, H. *Top. Stereochem.* 7 (1973) 295.
- Jensen, K. A. and Henriksen, L. *Acta Chem. Scand.* 22 (1968) 1107.
- Gompper, R. and Töpff, W. *Chem. Ber.* 95 (1962) 2871.
- Henriksen, L. and Autrup, H. *Acta Chem. Scand.* 24 (1970) 2629.
- Bock, H., Wagner, G., Wittel, K., Sauer, J. and Seebach, D. *Chem. Ber.* 107 (1974) 1869.
- Rosenberg, A. and Devlin, J. P. *Spectrochim. Acta* 21 (1965) 1613.
- Cope, A. C. and Hoyle, K. E. *J. Am. Chem. Soc.* 63 (1941) 733.
- Schuijl, P. J. W., Brandsma, L. and Arens, J. F. *Recl. Trav. Chim. Pays-Bas* 85 (1966) 1263.
- Dittmer, D. C., Simmons, H. E. and Vest, R. D. *J. Org. Chem.* 29 (1964) 497.
- Jensen, K. A. and Henriksen, L. *Acta Chem. Scand.* 24 (1970) 3213.
- Ericsson, E., Sandström, J. and Wennerbeck, I. *Acta Chem. Scand.* 24 (1970) 3102.
- Betteridge, D., Baker, A. D., Bye, P., Hasannudin, S. K., Kemp, N. R. and Thompson, M. J. *Electron Spectrosc. Rel. Phenom.* 4 (1974) 163.
- Bye, P. and Betteridge, D. J. *Electron Spectrosc. Rel. Phenom.* 7 (1975) 355.
- Nelander, B. *Theor. Chim. Acta* 25 (1972) 382.
- Santry, D. P. and Segal, G. A. *J. Chem. Phys.* 47 (1967) 158.
- Klewe, B. and Seip, H. M. *Acta Chem. Scand.* 26 (1972) 1860.
- Kapecki, J. A., Baldwin, J. E. and Paul, I. C. *Tetrahedron Lett.* (1967) 5307.
- Bock, H. and Stafast, H. *Chem. Ber* 105 (1972) 1158.
- Baker, A. D., Baker, C., Brundle, C. R. and Turner, D. W. *Int. J. Mass. Spectrom. Ion. Phys.* 1 (1968) 285.
- Stafast, H. and Bock, H. *Tetrahedron* 32 (1976) 855.
- Dewar, M. J. S. In *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York 1969, Chapter 6.
- Taylor, H. S. and Glasstone, S. *A Treatise on Physical Organic Chemistry*, Part I, D. Van Nostrand Co., 3rd Ed., New York 1942, p. 287.
- Brownlee, R. T. C. and Taft, R. W. J. *Am. Chem. Soc.* 92 (1970) 7007.
- Brownlee, R. T. C. and Taft, R. W. J. *Am. Chem. Soc.* 90 (1968) 6537.
- Abrahamsson, S., Rehnberg, G., Liljefors, T. and Sandström, J. *Acta Chem. Scand. B* 28 (1974) 1109.
- Henriksen, L. *To be published.*

Received July 12, 1976.