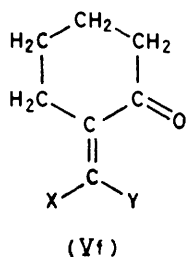
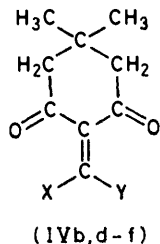
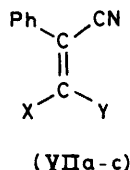
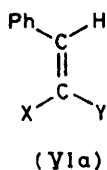
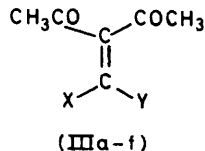
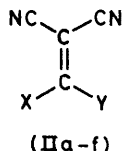
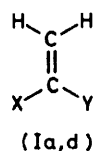


The Effects of Double-bond Twisting on the Photoionization Energies of Push-pull Ethylenes

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The u.v. photoelectron spectra of a number of push-pull substituted ethylenes with two donor groups and with planar or twisted double bonds have been interpreted by the aid of perturbational arguments, CNDO/2 calculations, and comparison with published spectra of similar compounds. The highest bonding molecular orbital in all cases is of π -type, and its energy is raised with increasing twist about the double bond, whereas the orbital formed by anti-symmetric combination of the donor atom p_z orbitals is unchanged or lowered by increased twist. Through-bond interaction splits the 'non-bonding' oxygen orbitals by 0.6–0.7 eV in 1,1-diacetyl-2,2-diaminoethylenes, in which the carbonyl groups are *E,Z* oriented with respect to the C=C double bond. When *Z,Z* orientation is enforced by ring closure, the splitting is only 0.38 eV, in agreement with calculations. In the 2,2-dithio-analogues, interaction with the C-S bond orbitals leads to a more complex splitting pattern.

ETHYLENES with strong donor groups on one carbon atom and strong acceptors on the other ('push-pull' ethylenes) and with sufficient steric interactions between these groups are permanently twisted around the



- a; X = Y = N(CH₃)₂
b; X, Y = CH₃N(CH₂)₂NCH₃
c; X, Y = CH₃N(CH₂)₃NCH₃
d; X = Y = S(CH₃)₃
e; X, Y = S(CH₂)₂S
f; X, Y = S(CH₂)₃S

carbon-carbon double bond, as has been demonstrated by ¹H n.m.r.¹ and by X-ray crystallography.² We now report the results of an investigation by u.v. photoelectron spectroscopy of some twisted ethylenes and some planar analogues performed in order to study the effect of the twist on the electron energy levels. The new

compounds studied are (IIIa–f), (IVb), (IVd–f), (Vf), (VIa), and (VIIa–c), whereas the spectra of (Ia and d)³ and (IIa–f)⁴ have been taken from the literature.

Compounds (IIIb and c), (IVb), and (VIIc) have twisted double bonds,^{1,5} and this may also apply to (VIIb), whereas the other molecules probably have the double bond and the directly bonded atoms in one plane. The angle of twist increases on going from (IIIb) to (IIIc) or from (VIIb) to (VIIc) due to the increased steric effect.⁵ In all bisdimethylaminoethylenes the dimethylamino-groups are rotated out of the plane due to steric interaction between the two *E*-methyl groups (*cf.* tetramethylthiourea⁶).

EXPERIMENTAL

Materials.—The synthesis of compounds (IIIa, b, d, and f), (VIa), and (VIIa and b) is described in the literature (for references see Table). The remaining compounds have been prepared by analogous methods, the details of which will be published elsewhere.⁷

Photoelectron Spectra.—These were recorded on a Perkin-Elmer PS 18 photoelectron spectrometer. The spectra were calibrated using the Ar and Xe lines. Reproducibility was ± 0.03 eV. The results are given in the Table.

CNDO/2 Calculations.—These were performed with the standard program of Pople and Beveridge.⁸ Calculations on the sulphur-containing compounds were performed without inclusion of *d* orbitals, using a revised program.^{9,10} The geometries in general are taken from ref. 11. The calculation on (IIIb) was performed with a dihedral angle at the 'double bond' of 45°, and the length of this bond was taken to be 1.45 Å in agreement with an X-ray structure.² The geometric data used in the calculations on (VIIa) follow from the Table, footnote *g*.

RESULTS AND DISCUSSION

The photoelectron (p.e.) spectra of the 1,1-diacetyl compounds (III) in general display four bands (IE_1 —

⁶ W. A. Spofford, E. A. H. Griffith, and E. L. Amma, *Chem. Comm.*, 1970, 533.

⁷ J. Sandström and U. Sjöstrand, *Tetrahedron*, in the press.

⁸ J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory', McGraw-Hill, New York, 1970, Appendix A.

⁹ D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 1967, **47**, 158.

¹⁰ B. Nelander, *Theor. Chim. Acta*, 1972, **25**, 382.

¹¹ E. Ericsson, T. Marnung, J. Sandström, and I. Wennerbeck, *J. Mol. Structure*, 1975, **24**, 373.

¹ J. Sandström and I. Wennerbeck, *Chem. Comm.*, 1971, 1088.

² S. Abrahamsson, G. Rehnberg, T. Liljefors, and J. Sandström, *Acta Chem. Scand.*, 1974, **B28**, 1109.

³ H. Bock, G. Wagner, K. Wittel, J. Sauer, and D. Seebach, *Chem. Ber.*, 1974, **107**, 1869.

⁴ D. Betteridge, L. Henriksen, J. Sandström, I. Wennerbeck, and M. A. Williams, *Acta Chem. Scand.*, 1977, **A31**, 14.

⁵ J. Sandström, U. Sjöstrand, and I. Wennerbeck, *J. Amer. Chem. Soc.*, 1977, **99**, 4526.

IE₄) with ionization energies below 10 eV, though all bands are not always resolved (Figure 1). A recent study of the p.e. spectra of a series of 1,1-dicyanoethylenes (II) with a variety of donors in the 2-position⁴ led to the assignment of the lowest IE to ionization from the highest π -orbital (π_1), and the following one to the antisymmetric combination of the donor atom p_z^* orbitals (n_-). The broadness of the first band in all compounds (III)—(VII) supports its assignment to ionization from the corresponding π -type orbital (π_1), the reduction of the IE value on going from series (II) to series (III) being in agreement with the smaller electron-withdrawing ability of the acetyl compared with the cyano-group (*cf.* IE₁ 10.1 in benzonitrile and 9.55 eV in acetophenone¹²). Besides this and the n_- band, the 1,1-diacetyl compounds should have low-energy bands due to the 'lone-pair' orbitals on the oxygen

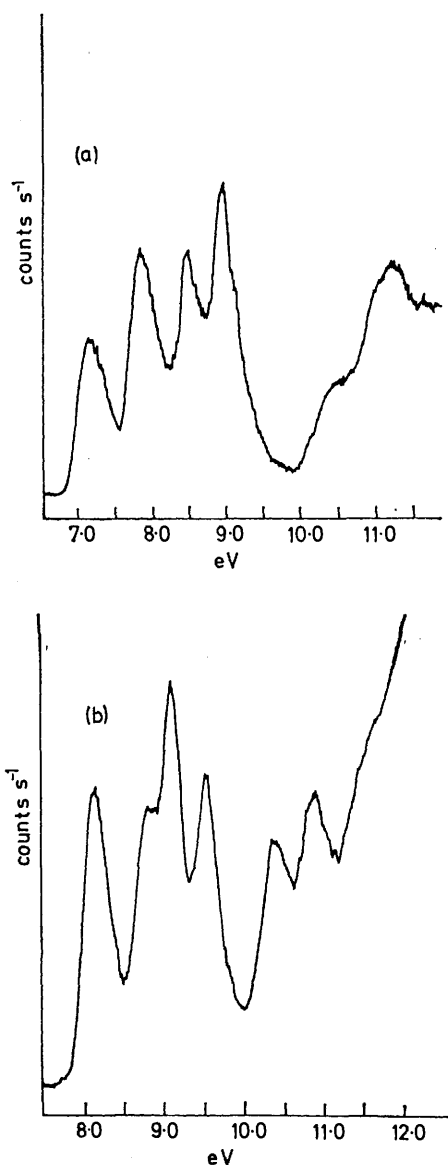


FIGURE 1 (a) and (b).

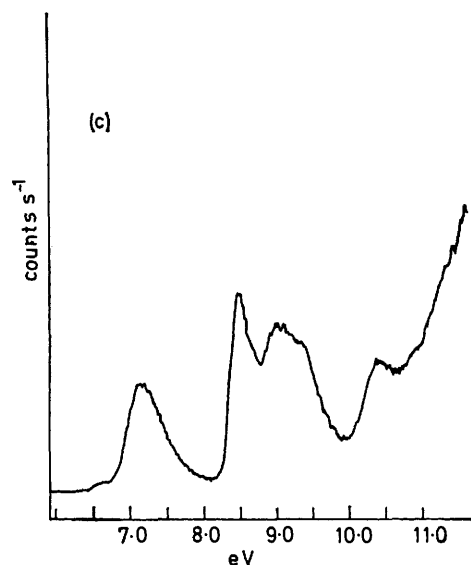
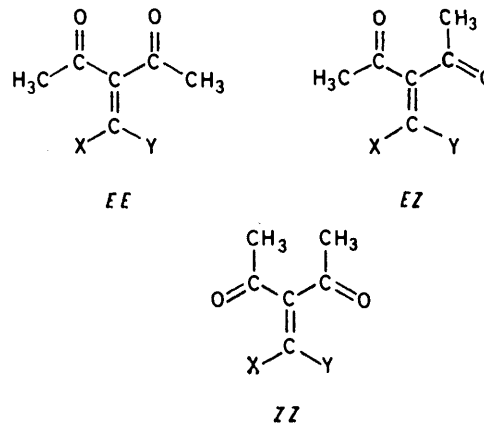


FIGURE 1 P.e. spectra of (a) IIIc, (b) IIIf, and (c) VIIa

atoms. The splitting by through-bond coupling of these orbitals in carbonyl groups separated by one, two, or three bonds has been discussed by Swenson and Hoffmann,¹³ and experimental splittings of 0.6–0.7 eV by coupling over two bonds have been reported.^{14,15} It



is evident that the magnitude of the coupling is influenced by the geometric arrangement of the carbonyl groups. In 1,1-diacetylenes three conformations have to be taken into account. Considerations of dipole-dipole interactions favour the *EZ* and disfavour the *EE* form, and the same result is found by analysis of CNDO/2 calculations and of the dipole moment of (IIIa).¹¹ Low temperature ¹H n.m.r. spectra of (IIIa) show only the *EZ* form, whereas (IIIb and c) appear as mixtures of *EZ* and *ZZ* forms in ratios of *ca.* 2 : 1 in

* The main molecular plane is in the *xy* plane.

¹² T. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Japan*, 1974, **47**, 2563.

¹³ J. R. Swenson and R. Hoffmann, *Helv. Chim. Acta*, 1970, **53**, 2331.

¹⁴ D. O. Cowan, R. Gleiter, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem.*, 1971, **83**, 405.

¹⁵ A. Schweig, H. Vermeer, and U. Weidner, *Chem. Phys. Letters*, 1974, **26**, 229.

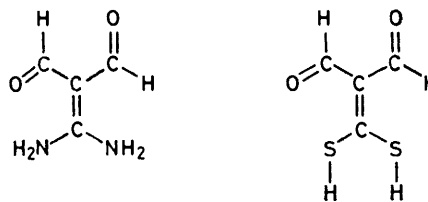
Experimental and calculated (CNDO/2) ionization energies and assignments

Compound	IE _{exp} /eV ^a	IE _{calc} /eV ^b	Assignment	Ref ^c
(IIIa)	7.61		π_1	<i>h</i>
	8.3sh		$n(O)_-$	
	8.47		$n(N)_-$	
	9.04		$n(O)_+$	
	10.64			
(IIIb)	7.32	9.45 ^d	π_1	<i>h</i>
	7.95	10.90	$n(O)_-$	
	8.57	11.70	$n(O)_+$	
	8.92	12.88	$n(N)_-$	
	10.60	14.11	π_2 ^e	
(IIIc)	7.13		π_1	7
	7.80		$n(O)_-$	
	8.44		$n(O)_+$	
	8.90		$n(N)_-$	
	10.5		π_2	
(IIId)	8.50		π_1	<i>i</i>
	9.16 ^f		$n(O)_-, n(S)_-$	
	9.85		$n(O)_+$	
	10.34		π_2	
(IIIe)	8.28	11.23	π_1	7
	8.9sh	11.64	$n(O)_-$	
	9.16	12.43	$n(S)_-$	
	9.63	12.71	$n(O)_+$	
	10.92	13.00	σ	
(IIIf)	11.50	14.79	σ	11
	8.15	11.16	π_1	
	8.9sh	11.17	$n(O)_-$	
	9.17	12.51	$n(S)_-$	
	9.62	12.74	$n(O)_+$	
(IVb)	10.56			7
	11.07			
	7.48		π_1	
	7.96		$n(O)_-$	
(IVd)	8.34		$n(O)_+$	7
	8.79		$n(N)_-$	
	8.21		π_1	
	8.60		$n(S)_-$	
(IVe)	8.8sh		$n(O)_-$	7
	9.45		$n(O)_+$	
	8.32		π_1	
	8.61		$n(O)_-$	
(IVf)	8.98		$n(S)_-$	7
	9.22		$n(O)_+$	
	8.11		π_1	
	8.53		$n(S)_-$	
(Vf)	8.8sh		$n(O)_-$	7
	9.33		$n(O)_+$	
	8.07 ^f	10.82, 10.99	$\sigma(C-S), \pi_1$	
	8.61	12.25	$n(S)_-$	
(VIa)	8.87	12.55	$n(O)$	<i>j</i>
	6.89		π_1	
	8.01		$n(N)_-$	
	8.81		A_2	
(VIIa)	9.0sh		π_2	<i>h</i>
	10.22		π_3	
	7.20		π_1	
	8.50		$n(N)_-$	
	9.02		A_2	
(VIIb)	9.4sh		π_2	<i>h</i>
	10.4		π_3	
	7.10		π_1	
	9.01 ^f		$n(N)_-, A_2$	
(VIIC)	9.2sh		π_2	7
	6.85	8.91 ^g	π_1	
	8.72 ^f	12.41, 13.61	π_2, A_2	
	9.0sh	12.59	$n(N)_-$	

^a Vertical ionization energy. ^b Assuming the validity of the Koopmans theorem. ^c For preparation. ^d Calculated with a C=C dihedral angle of 45° and a bond length of 1.45 Å. ^e Localized in the Ac₂C part. ^f Two overlapping bands. ^g Calculated with a C=C dihedral angle of 30°, a Ph-C dihedral angle of 60°, and a C=C bond length of 1.43 Å. ^h E. Ericsson, J. Sandström, and I. Wennerbeck, *Acta Chem. Scand.*, 1970, **24**, 3102. ⁱ J. Sandström and I. Wennerbeck, *Acta Chem. Scand.*, 1970, **24**, 1191. ^j H. Weingarten and W. A. White, *J. Org. Chem.*, 1966, **31**, 2874.

deuteriochloroform solution.⁷ It therefore seems reasonable to assume that the *EZ* form dominates in the gas phase in all the 1,1-diacetyl compounds (III).

CNDO/2 calculations have been performed on the simplified model (VIII), and splittings of *ca.* 1.6, 0.9, and 0.4 eV between the 'lone pair' orbitals on the oxygen atoms have been found for the *EE*, *EZ*, and *ZZ*



(VIII)

(IX)

forms respectively. These splittings are rather independent of the angle of twist (Figure 2) and very little

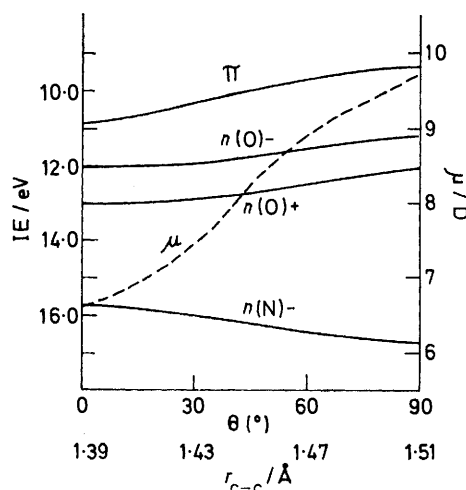


FIGURE 2 Calculated orbital energies (—) and dipole moment (---) of the *EZ* form of (VIII) versus dihedral angle and bond length of the C=C bond

interaction between the oxygen lone pair orbitals and the C-N σ orbitals is indicated by the calculations even for the planar molecule, probably due to the rather large energy gap. The overlap integrals and Hartree-Fock matrix elements show that even in the *EE* form the through-space interaction between the oxygen orbitals is negligible. Instead, a through-bond coupling takes place by interaction with the antisymmetric and symmetric combinations of the intervening C-C bonds (Figure 3). As proposed in ref. 13, the resulting antisymmetric orbital, $n(O)_-$, has higher energy than the symmetric orbital $n(O)_+$.

Assuming that IE₁ is due to ionization from the highest π MO and that the splitting between $n(O)_-$ and $n(O)_+$ is fairly constant in the series (IIIa—c), the assignment of the four bands with lowest IE is straightforward. For compound (IIIa), the order is π_1 , $n(O)_-$, $n(N)_-$,* and

* $n(N)_-$ stands for the antisymmetric combination of the donor p_z orbitals.

$n(O)_+$, whereas for (IIIb and c) the order is π_1 , $n(O)_-$, $n(O)_+$, and $n(N)_-$. These assignments are in agreement with the results of CNDO/2 calculations (Table). The relatively low IE of $n(N)_-$ in (IIIa) is in agreement with the findings in the 1,1-dicyano-analogues (II).⁴

The spectrum of (IVb) shows a splitting of only 0.38 eV between IE_2 , $n(O)_-$, and IE_3 , $n(O)_+$, in good agreement with the calculated value. The lowering of π_1 and the raising of $n(N)_-$ when going from the *EZ* to the *ZZ* form is also reproduced by the calculations.

Calculations on the simple model (IX) indicate that $n(O)_-$ and $n(O)_+$ in (III d–f) and (IV d–f) are split by interaction with the antisymmetric and symmetric combinations of the C–S σ orbitals. This leads to five rather high lying orbitals, and also to an increased splitting between $n(O)_-$ and $n(O)_+$. Also in this case the calculated splitting is smaller in the *ZZ* than in the *EZ* form.

Under similar assumptions as for the nitrogen analogues one arrives at the order π_1 , $n(O)_-$, $n(S)_-$, $n(O)_+$ for

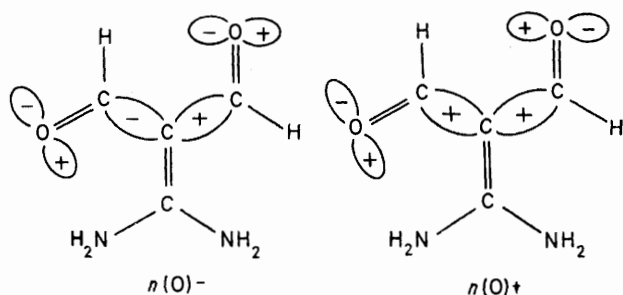


FIGURE 3 Through bond coupling of the oxygen lone pair orbitals in the *EZ* form of (VIII)

(III d–f). The same order fits the spectrum of (IVe), whereas a decreased $n(O)-n(O)_-$ splitting requires the order π_1 , $n(S)_-$, $n(O)_-$, $n(O)_+$ for (IV d and f). This, however, implies a strong upward shift of $n(S)_-$ compared with (III d and f), for which we at present have no explanation, though both calculations and experiments indicate higher $n(S)_-$, $n(O)_-$, and $n(O)_+$ levels in the *ZZ* than in the *EZ* form. The assignments are also supported by the shapes of the bands.

In the spectrum of (Vf), ionizations from four orbitals with $IE < 9$ eV can be seen, the two lowest IE bands overlapping. Of these four, π_1 probably has one of the lowest IE and $n(S)_-$ one of the two highest. The other two orbitals are combinations of the C=O and S–C–S σ orbitals, the highest one having mostly symmetrical S–C–S character and the other mostly oxygen lone pair character.

The effect of increased twist about the double bond can be observed by a comparison of the spectra of (IIIb and c). According to calculations on model (VIII), the π_1 , $n(O)_-$, and $n(O)_+$ energies should be raised and that

of $n(N)_-$ should be lowered by increased twist (Figure 2). These effects can be understood on the basis of the increased charge separation, the donor part becoming more positive and the acceptor part more negative on rotation. An increased localization of π_1 in the acceptor part is also indicated by the calculations.

The prediction for the first three IEs is seen to be fulfilled, (ΔIE_1 0.19, ΔIE_2 0.15, ΔIE_3 0.13 eV, all positive when IE decreases from b to c), whereas IE_4 is nearly unaffected (ΔIE_4 0.02 eV). These results, however, can also be explained by the stronger donor capacity of the six- than of the five-membered ring. A comparison with the analogues (IIb and c), where no double-bond twist occurs, shows a ΔIE for π_1 of 0.09 eV and for $n(N)_-$ of 0.18 eV. The larger ΔIE values for π_1 and the smaller for $n(N)_-$ for (IIIb and c) are in the expected direction for an effect of larger twist angle. It may be noted that twisting of a non-polar double bond also leads to a lowering of the IE of the highest occupied π MO, though the rationale for this is different.¹⁶

The effect of the donor groups on π_1 in (III d–f) parallels the effects on the highest MO in the analogous trithiocarbonates¹⁷ and reflects an increasing donor capacity in the series SCH_3 , $SCH_3 < SCH_2CH_2S < SCH_2CH_2CH_2S$.

The spectrum of VIa can be rationalized by a comparison with those of styrene¹⁸ and 1,1-bisdimethylaminoethylene (Ia).³ The lowest IE in styrene, 8.42 eV, is ascribed to a π -orbital with a 65% contribution from the B_1 orbital in the benzene ring and a 35% contribution from the bonding ethylenic π -orbital, these two orbitals being combined in opposite phase. The second IE, 9.13 eV, is ascribed to the benzene A_2 orbital, largely unaffected by the substitution, and the third, 10.55 eV, to a π -orbital mainly localized in the ethylenic double bond. Assuming the energy of the nitrogen p_z orbitals to be the same as that of the $n(N)_-$ orbital in (Ia), 8.2 eV,³ a correlation diagram can be constructed, according to which IE_1 in (VIa) is due to ionization from a π -orbital, which is a combination of the highest styrene π -orbital and $n(N)_+$ in opposite phase. IE_2 is ascribed to $n(N)_-$, and IE_3 and IE_4 to either of the benzene A_2 orbital and the in-phase combination of the highest styrene π -orbital and the $n(N)_+$ orbital. The sharp band at 10.22 eV in (VIa) may have a strong contribution from the third π -orbital of the styrene part.

Introduction of a cyano-group in the 1-position is assumed to stabilize the highest bonding orbitals primarily by an inductive effect. It seems reasonable that the in-phase and out-of-phase combinations of the highest bonding styrene π -orbital and $n(N)_+$ should be stabilized by about equal energy quantities, which places the lower of these (π_2) below the benzene A_2 orbital in (VIa) and (VIIa).

The p.e. spectra of (VIIb and c) show an isolated

¹⁷ C. Guimon, D. Gonbeau, G. Pfister-Guillouzo, L. Åsbrink, and J. Sandström, *J. Electron Spectroscopy*, 1974, 4, 49.

¹⁶ C. Batich, O. Ermer, E. Heilbronner, and J. R. Wiseman, *Angew. Chem.*, 1973, 85, 302.

¹⁸ J. W. Rabalais and R. J. Colton, *J. Electron Spectroscopy*, 1972–1973, 1, 83.

band with low IE (7.10 and 6.85 eV) followed by a group of three poorly resolved bands around 9 eV. The low IE band is assigned to π_1 , and $\Delta IE = 0.25$ eV reflects an increased angle of twist in (VIIC). In both compounds a shoulder at 9.0 eV is assigned to the $n(N)_-$ orbital, in good agreement with the attribution of the 8.50 eV band in (VIIa) to the same orbital.

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