A Theoretical Conformational Study of Push–Pull Ethylenes. Part 1. Substituted Methyleneimidazolidines

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Geometries, polarisations, torsional barriers, ionisation potentials, and dipole moments have been computed by MNDO-type calculations for a representative group of 'push–pull' ethylenes, formed by an imidazoline ring and a series of acceptor substituents to the double bond, such as cyano, acetyl, and phenyl groups. A relevant number of geometrical parameters was included in the conformational energy optimisation procedure. The comparison with the set of available experimental data allows a rationalisation of the role of π- and strain-energy contributions to the conformational stabilities, and the effect of the withdrawing power of substituents on the height of the barrier.

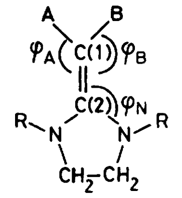
It has long been known that suitable substituents can lower the energy barrier of *cis–trans* isomerisation of an olefin. The potential energy curve for the rotation around the double bond can be regarded as the sum of two potential energy curves, one for π-electron energy and the other for steric strain.[1] The former has its maximum at the dihedral angle $\omega = 90°$, the latter at $\omega = 0°$, due to non-bonded repulsions between the substituents on the two carbon atoms. The ground state will be found at the minimum of the sum of these potential energy curves; the position of this minimum is dependent on the shapes of the potential energy curves. The passage between the two enantiomeric minima may occur *via* either a twisted or a planar transition state. The barriers to these two processes are referred as the π barrier (E_π) and steric barrier (E_S), respectively.

In 'push–pull' ethylenes strong acceptors on one carbon atom and strong donors on the other lower E_π, due to the stabilisation of the zwitterionic transition state, and increase E_S when strong steric effects are present.

In the present paper we report a theoretical study of conformational properties and electronic structures on a variety of substituted methyleneimidazolidines (**1**)—(**12**), for which experimental static and dynamic data are available.

The crystal structure of (**2**),[2] (**7**) (derivative),[3] (**8**),[4] and (**9**)[4] have been determined and C=C bond lengths between 1.407 and 1.466 Å have been observed with rotation angles of 20.2, 41.1, 4.9, and 72.9°, respectively. Experimental dipole moments are reported for (**2**) (7.93 D[5]) and for a derivative of (**11**) (6.54 D[5]). The former agrees with the value calculated by CNDO/2 method and the analysis of the charge distribution shows that *ca.* 0.5 electrons are transferred from the donor (imidazoline ring) to the acceptor side [$C(CN)_2$ group] of the molecule.

Information about the energies of the occupied orbitals in the ground state for (**2**),[6] (**5**), and (**9**)[7] is derived from photoelectron spectra, accepting the approximate validity of Koopmans' theorem. According to CNDO/2 calculations, the lowest IP is ascribed in all cases to ionisation from the highest occupied orbital, with a large contribution from the symmetric combination of donor p_z orbitals. The second or higher IP refers to ionisation from the antisymmetric combination of donor p_z orbitals. The energy of the former IP is lowered by increasing twist about the C=C bond, unlike the energy of the latter which remains practically unchanged or increases on increasing twist.



	R	A	B
(**1**)	H	CN	CN
(**2**)	CH_3	CN	CN
(**3**)	Bu^t	CN	CN
(**4**)	H	CN	Ph
(**5**)	CH_3	CN	Ph
(**6**)	H	CN	$COCH_3$
(**7**)	CH_3	CN	$COCH_3$
(**8**)	H	$COCH_3$	$COCH_3$
(**9**)	CH_3	$COCH_3$	$COCH_3$
(**10**)	H	$COCH_3$	Ph
(**11**)	CH_3	$COCH_3$	Ph
(**12**)	CH_2Ph	$COCH_3$	COPh

The influence of steric and electronic factors on the rotational barriers of several push–pull ethylenes was investigated by dynamic n.m.r. For most compounds investigated only $\Delta G^{\ddagger}$ values at coalescence temperature are available. However, there are indications[1] that, at least for series of related systems, $-\Delta S^{\ddagger}$ increases with $\Delta H^{\ddagger}$. In such cases $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ values are proportional and a comparison with the calculated energy barriers is acceptable.

The following data are available: compound (**5**), $\Delta G^{\ddagger}$ 9.5 kcal mol^{-1} at 190 K;[8] *p*-methyl and *p*-chloro analogues: $\Delta G^{\ddagger}$ 10.0 and 9.1 kcal mol^{-1} at 204 and 186 K respectively;[9] $\Delta G_S^{\ddagger}$ should be small since the aryl group must be nearly orthogonal to the double bond on passage over the steric barrier. Compound (**9**): only the free energy barriers for acetyl rotations were determined by dynamic n.m.r.,[10] $\Delta G^{\ddagger}(EZ \rightarrow ZZ)$ 12.3 kcal mol^{-1}, and $\Delta G^{\ddagger}(EZ \rightarrow EE)$ 13.4 kcal mol^{-1} at 240 K. The spectrum observed in $CHCl_2F$ at 206 K was interpreted as due to *ZZ* and *EZ* forms with fractional populations of 0.33 and 0.67, respectively. However, the value of the barrier for the rotation of C=C through the planar transition state ($\Delta G_S^{\ddagger}$) of the *ZZ* conformer would be not significantly different from that of compound (**12**), for which the following data were found at 332 K in *o*-dichlorobenzene: $\Delta G_S^{\ddagger}$ 16.6 kcal mol^{-1}; $\Delta H_S^{\ddagger}$ 19.2 kcal mol^{-1}; and $\Delta S_S^{\ddagger}$ 7.7 cal mol^{-1} K^{-1}.[11] Compound (**11**): a free energy barrier of 11.5 kcal mol^{-1} was reported[10] for $Z \rightarrow E$

Table 1. MNDO geometrical parameters for push–pull ethylenes

Compound	Conformer	ω	C=C	C-A/C-B	C-N ring	φ_A/φ'_B	φ_N
(1)		**0**	1.391	1.418	1.392	121.8	127.3
		90	1.436	1.400	1.377	119.2	126.5
(2)		**0**	1.393	1.423	1.408	124.8	127.1
		90	1.441	1.401	1.385	119.3	125.8
(3)		0	1.402	1.428	1.407	128.5	128.1
		70.4	1.434	1.408	1.399	121.5	126.3
		90	1.446	1.403	1.390	120.3	125.6
(4)		**0**	1.372	1.424/1.491	1.422	121.4/123.3	126.0
		90	1.432	1.406/1.406	1.400	113.6/123.1	124.7
(5)		**0**	1.382	1.424/1.494	1.402	123.8/126.8	128.8
		90	1.442	1.406/1.461	1.379	113.6/123.3	127.6
(6)	*Z*	**0**	1.400	1.421/1.485	1.388	117.1/125.3	128.1
		90	1.441	1.402/1.457	1.371	116.4/119.1	127.2
	E	0	1.392	1.428/1.492	1.395	115.5/130.3	128.1
		90	1.434	1.408/1.460	1.373	114.8/124.2	127.3
(7)	*Z*	0	1.404	1.429/1.496	1.417	118.2/131.3	127.4
		47.5	1.416	1.415/1.478	1.403	117.6/123.4	127.3
		90	1.446	1.403/1.457	1.380	119.2/121.1	126.3
	E	49	1.408	1.421/1.484	1.407	116.8/126.9	127.4
		90	1.499	1.408/1.460	1.387	114.7/124.5	128.0
(8)	*ZZ*	0	1.425	1.492	1.394	118.4	128.4
		46.2	1.434	1.478	1.385	116.1	127.4
		90	1.459	1.451	1.372	114.1	126.9
	EE	0	1.387	1.517	1.403	122.6	128.9
		49.9	1.409	1.492	1.391	120.2	127.7
		90	1.434	1.470	1.377	119.1	127.3
	EZ	0	1.403	1.500/1.510	1.408	123.1/118.4	121.6
		44.7	1.417	1.487	1.386	118.7	128.0
		90	1.445	1.465	1.373	116.8	127.3
(9)	*ZZ*	0	1.429	1.507	1.425	121.7	128.6
		80	1.461	1.462	1.382	114.4	126.3
		90	1.463	1.461	1.381	114.3	126.2
	EE	79.8	1.453	1.473	1.387	119.3	126.6
		90	1.440	1.471	1.386	119.2	126.5
		80	1.449	1.462/1.472	1.384	119.9/114.3	126.4
	EZ	90	1.452	1.542/1.466	1.382	116.4/116.4	126.8
(10)	*Z*	0	1.380	1.495/1.496	1.430	117.6/124.5	125.9
		4	1.382	1.495/1.492	1.419	117.4/124.6	124.5
		90	1.437	1.477/1.446	1.406	116.9/118.1	126.5
	E	0	1.372	1.502/1.504	1.429	117.2/128.8	126.5
		4	1.373	1.501/1.503	1.428	117.2/128.5	126.4
		90	1.425	1.485/1.450	1.379	115.4/124.3	127.4
(11)	*Z*	0	1.393	1.502/1.499	1.430	119.6/129.5	127.5
		41.3	1.405	1.490/1.483	1.414	119.4/122.1	126.7
		90	1.440	1.483/1.449	1.399	118.1/118.5	125.7
	E	43	1.396	1.496/1.492	1.417	119.2/125.3	126.2
		90	1.431	1.491/1.452	1.402	117.0/123.9	126.0

Distances in Å and angles in degrees.

acetyl change. The torsional barrier around the C=C bond ($\Delta G^{\ddagger}$) would be larger for **(11)** than for **(9)**, as found for 2,2-bis(dimethylamino)ethylene analogues.[12]

Theoretical calculations on preferred conformations and rotation energy barriers have not so far been performed. According to CNDO/2 calculations[5] for compound **(5)**, the length of the C=C bond only was obtained by energy minimisation; standard values were adopted for the other bond lengths and angles.

Calculations

Total energy of each considered molecule was computed by the standard MNDO method,[13] using QCPE program no. 353. In fact, it was observed that *ab initio* SCF calculations with a minimal Slater basis set fail in predicting the rotation barrier of ethylene.[14] Values of good accuracy were obtained only by using contracted gaussian DZ basis sets combined with an appropriate configuration interaction.[15] On the other hand, MINDO(3) and MNDO semiempirical SCF calculations appear reliable in predicting the rotation barrier of ethylene[16] (63.9[16] and 62.5[13] kcal mol^{-1}, respectively).

An energy-minimisation procedure which iteratively optimises the most relevant geometrical parameters through an interpolation process till the desired self-consistency was achieved, was carried out.[17,18] The large number of geometrical variables prevented full energy optimisation. However, all the geometrical parameters directly or indirectly affecting the conformation were left to vary freely. The torsional angle of the acetyl group, fixed at $\varphi = 0$, was the only exception. The limitation was necessary as the method typically favours structures with the two conjugated parts of the system perpendicular, or nearly perpendicular.[19] Really, experimental evidence[4] indicates a nearly planar conformation for the acetyl

Table 2. Relevant MNDO energies, dipole moments, and charges for push–pull ethylenes

Compound	Conformer and symmetry	ω(°)	$\Delta H_f°$/kcal mol^{-1}	E_π/kcal mol^{-1}	E_S/kcal mol^{-1}	IP(eV)	μ(D)	q[C(1)]	q[C(2)]	CT
(1)	C_{2v}	0	76.4	19.7		8.98 $\pi_1(B_2)$	7.73	−0.18	+0.40	0.53
(2)	C_{2v}	~0	86.0	11.6		8.92 $\pi_1(B_2)$	7.75	−0.17	+0.42	0.45
(3)	C_2	70.4	108.4	1.1	11.2	8.06 (B)	9.48	−0.38	+0.53	0.69
(4)		0	70.3	29.5		8.95 π_1	4.90	−0.11	+0.23	0.22
(5)		0	85.9	14.5		8.46 π_1	5.74	−0.22	+0.40	0.35
(6)	*Z*	0	8.6	13.7		8.92 π_1	5.32	−0.32	+0.43	0.49
	E	0	15.6	13.2		9.10 π_1	8.35	−0.25	+0.36	0.36
(7)	*Z*	47.4	20.6	3.7	8.9	8.58	5.97	−0.39	+0.49	0.57
	E	49.3	27.1	3.8	High	8.59	9.39	−0.36	+0.46	0.52
(8)	*ZZ*(C_2)	46.2	−46.6	3.7	3.5	8.61 (B)	3.38	−0.49	+0.49	0.61
	EZ	44.7	−43.7	3.8	3.4	8.66	7.17	−0.48	+0.47	0.51
	EE(C_2)	49.9	−37.8	4.8	4.1	8.56 (B)	10.25	−0.48	+0.45	0.50
(9)	*ZZ*(C_2)	80.0	−40.1	0.3	42.3	8.18 (B)	4.43	−0.59	+0.57	0.76
	EZ	80.0	−37.7	0.8	High	8.16	8.68	−0.60	+0.56	0.73
	EE(C_2)	79.8	−30.4	0.3	High	8.06 (B)	11.98	−0.61	+0.55	0.69
(10)	*Z*	4.2	7.3	23.9	0.3	8.77 π_1	3.39	−0.27	+0.28	0.28
	E	3.9	10.8	21.0	0.1	8.96 π_1	5.15	−0.22	+0.22	0.19
(11)	*Z*	41.3	24.4	7.2	8.2	8.13	4.38	−0.40	+0.43	0.44
	E	43.0	29.1	8.8	High	8.18	6.51	−0.36	+0.39	0.37

group, at least when steric hindrance effects are lacking in the molecular environment.

The geometry of the imidazoline ring was optimised for the conformations considered. However, symmetry and planarity constraints were retained throughout the calculations, by presuming slight modifications from planarity for the isolated system in the gas phase.

The most significant geometrical parameters for each molecule or conformation are collected in Table 1, referring to structures **(1)**—**(12)** for atom labelling. The full geometrical data are available upon request. Heats of formation, π (E_π), and strain (E_S) barriers, first ionisation potentials (IP), and dipole moments (μ) for ground state of each molecule are collected in Table 2, together with the most significant charge distribution parameters.

Results and Discussion

The geometrical parameters collected in Table 1 evidence some characteristic behaviour. The variation of C=C bonds depends both on the extent of the torsion angle ω and on the type of electron-acceptor substituents A,B. In particular, the substitution of a cyano group by phenyl produces a shortening of *ca.* 0.01—0.02 Å of the C=C bond length. The substitution of one cyano group by one acetyl group in the *Z* conformation lengthens the double bond by 0.01—0.02 Å, while no remarkable variations of the distance are observed when an acetyl group takes the *E*-conformation. The substitution of the N-H hydrogen atom by a methyl group determines an increase both of the torsional angle of the double bond, and of φ_A (or φ_B) and φ_N angles.

A detailed comparison between theoretical and experimental geometries of compound **(2)** is shown in Table 3. On the whole the agreement is satisfactory. The computed values are larger for C(4)-N(3) and C(6)-C(7) bonds, and shorter for C(1)$\hat{C}$(3)C(2) and N(3)$\hat{C}$(4)N(4) angles than experimental values. A rotation of ω = 20.2° about the C=C bond is found in the crystal, while a practically planar conformation (ω = 0) is predicted by MNDO calculations. However, the energy differences among conformations with torsional angles within $0 < \omega < 20°$ are < 1 kcal mol^{-1}. The envelope conformation of the imidazoline ring, with C(7) out of the molecular plane,[2] is not expected for the isolated molecule, as would be due to the packing of molecules in the crystal unit cell. The variation of the C=C distance is due more to the push–pull effect than to torsion of the double bond.

Table 3. Geometrical parameters of compound **(2)** [(**a**)]

	Exp.[a]	Calc.
Bond distances (Å)		
N(1)–C(1); N(2)–C(2)	1.148	1.163
C(1)–C(3); C(2)–C(3)	1.416	1.423
C(3)=C(4)	1.407	1.393
C(4)–N(3); C(4)–N(4)	1.345	1.408
N(3)–C(5); N(4)–C(8)	1.458	1.466
N(3)–C(6); N(4)–C(7)	1.467	1.447
C(6)–C(7)	1.495	1.531
Bond angles (°)		
C(1)–C(3)–C(2)	115.7	110.5
C(1)–C(3)–C(4); C(2)–C(3)–C(4)	122.1	124.8
C(3)–C(4)–N(3); C(3)–C(4)–N(4)	124.7	127.1
N(3)–C(4)–N(4)	110.5	105.8
C(4)–N(3)–C(5); C(4)–N(4)–C(8)	125.2	128.3
C(4)–N(3)–C(6); C(4)–N(4)–C(7)	109.4	112.8
C(5)–N(3)–C(6); C(8)–N(4)–C(7)	118.1	118.9
N(3)–C(6)–C(7); N(4)–C(7)–C(6)	102.8	104.3
Torsion angles (°)		
C(1)–C(3)–C(4)–N(3)	21.5	0
C(2)–C(3)–C(4)–N(4)	17.4	
C(4)–N(3)–C(6)–C(7)	16.6	0
C(4)–N(4)–C(7)–C(6)	20.9	
N(3)–C(6)–C(7)–N(4)	−21.6	0
C(7)–N(4)–C(4)–N(3)	−11.3	0
N(4)–C(4)–N(3)–C(6)	−3.8	

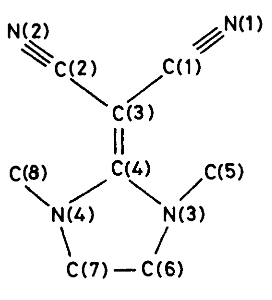
[a] Averaged values from ref. 2.

The geometries of compound **(8)** (*ZZ* conformation) and **(9)** (*EZ* conformation) are reported in Table 4 together with experimental data.[4] Owing to planarity constraints imposed by the acetyl groups of compound **(8)**, the rotation of the double bond is higher than the experimental value measured in the crystal. As the steric barrier is low (E_S 3.5 kcal mol^{-1}), partial torsion of the acetyl groups would probably favour conformations in which the double bond twist is reduced. Conformational energy calculations performed according to the molecular mechanics method[4] suggest that on steric grounds

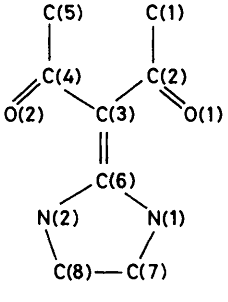
Table 4. Geometrical parameters of compounds (**8**) and (**9**) [(**b**) and (**c**)]

Compound (**8**) (*ZZ*) Exp.[a]	Compound (**8**) (*ZZ*) Calc.		Compound (**9**) (*EZ*) Exp.[a]	Compound (**9**) (*EZ*) Calc.
		Bond distances (Å)		
1.244	1.242	C(2)=O(1); C(4)=O(2)	1.237; 1.255	1.236; 1.244
1.505	1.530	C(1)–C(2); C(4)–C(5)	1.506; 1.501	1.540; 1.529
1.448	1.478	C(2)–C(3); C(3)–C(4)	1.433; 1.408	1.462; 1.472
1.451	1.434	C(3)=C(6)	1.468	1.449
1.327	1.385	C(6)–N(1); C(6)–N(2)	1.321	1.384
1.453	1.441	N(1)–C(7); N(2)–C(8)	1.455	1.452
1.532	1.548	C(7)–C(8)	1.513	1.540
		N(1)–C(9); N(2)–C(10)	1.454	1.471
		Bond angles (°)		
115.1	115.8	O(1)–C(2)–C(1); O(2)–C(4)–C(5)	117.0; 118.0	116.2; 117.5
121.4	119.6	O(1)–C(2)–C(3); O(2)–C(4)–C(3)	124.4; 120.9	123.3; 119.4
123.5	124.6	C(1)–C(2)–C(3); C(3)–C(4)–C(5)	118.5; 121.1	120.5; 123.1
125.4	127.8	C(2)–C(3)–C(4)	126.2	125.8
117.3	116.1	C(2)–C(3)–C(6); C(4)–C(3)–C(6)	118.5; 115.3	119.9; 114.3
125.6	127.4	C(3)–C(6)–N(1); C(3)–C(6)–N(2)	124.9; 124.6	126.4; 126.4
108.7	105.2	N(1)–C(6)–N(2)	110.5	107.2
112.8	114.4	C(6)–N(1)–C(7); C(6)–N(2)–C(8)	111.8	112.7
101.8	103.1	N(1)–C(7)–C(8); N(2)–C(8)–C(7)	103.0	103.7
		C(6)–N(1)–C(9); C(6)–N(2)–C(10)	127.0	125.9
		C(9)–N(1)–C(7); C(10)–N(2)–C(8)	121.3	121.3
		Torsion angles (°)		
6.8	0 [b]	C(1)–C(2)–C(3)–C(4)	−172.8	180 [b]
−172.7	180	C(1)–C(2)–C(3)–C(6)	5.3	0
14.9	0	C(5)–C(4)–C(3)–C(2)	0.8	0
−165.6	180	C(5)–C(4)–C(3)–C(6)	−177.4	180
−176.3	180	O(1)–C(2)–C(3)–C(4)	5.4	0
4.2	0	O(1)–C(2)–C(3)–C(6)	−176.5	180
−168.1	180	O(2)–C(4)–C(3)–C(2)	−180.0	180
11.4	0	O(2)–C(4)–C(3)–C(6)	1.9	0
−5.8	−46.2	C(2)–C(3)–C(6)–N(1)	73.4	80.0
175.7	133.8	C(2)–C(3)–C(6)–N(2)	−105.9	−100.0
174.7	133.8	C(4)–C(3)–C(6)–N(1)	−108.2	−100.3
−3.9	−46.2	C(4)–C(3)–C(6)–N(2)	72.4	79.7
173.7	180	C(3)–C(6)–N(1)–C(7)	179.2	180
174.8	180	C(3)–C(6)–N(2)–C(8)	−179.6	180
		C(3)–C(6)–N(1)–C(9)	3.5	4.5
		C(3)–C(6)–N(2)–C(10)	0.6	−2.0

[a] See ref. 4. [b] Assumed values.



(a)



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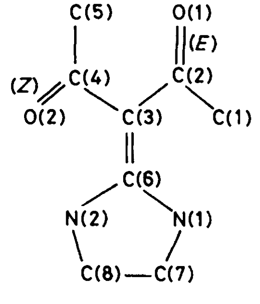

(c)

the system should be twisted by 22° in the free state. The presence of intra- and inter-molecular hydrogen bonds in the unit cell would contribute towards the nearly planar conformation in the crystalline phase.

In compound (**9**) the calculated twist angle about the C=C bond (80°) is slightly larger than the experimental value (72.9°). In the crystalline phase also the imidazoline ring is nearly planar, and the rotation of the acetyl groups around the C–C single bonds is much reduced in agreement with the constraints of the present calculations. In fact, hydrogen bonds are absent and the molecular conformation is determined by steric and push–pull effects only. The geometry differences between the two acetyl groups (*E* and *Z*) are correctly evaluated by calculations (Table 4), except for the C(2)–C(3) and C(3)–C(4)

Table 5. Experimental and calculated ionisation energies

Compound	IP(eV) Exp.	calc. MNDO		calc. CNDO/2	Assignment
(2)	8.20 [6]	8.92		9.81 [6]	$\pi_1(B_2)$
	9.51	10.61		12.73	$n_-(A_2)$
(5)	7.10 [7]	8.46			π_1
	9.01	10.21			$n(N)_-$
	9.2(sh)	9.23			π (benzene)
		9.29			
(9)	7.32 [7]	8.18	8.16	9.45 [7]	π_1
	7.95	9.61	9.46	10.90	$n(O)_-$
	8.57	10.09	9.93	11.70	$n(O)_+$
	8.92	10.66	10.90	12.88	$n(N)_-$
		(*ZZ*)	(*EZ*)	(*EZ*)	

distances. As for compound (**2**), also in (**8**) and (**9**) the calculated C_{sp^2}–N distances of the imidazoline ring are overestimated.

The analysis of calculated charge distributions (Table 2) shows that electron charge-transfer from the imidazoline ring to the acceptor side is increased by twisting about the C=C bond and by strong acceptor groups [CN ≈ $COCH_3$ (*Z*) > $COCH_3$ (*E*) > C_6H_5]. The calculated dipole moment for compound (**2**) (7.75 D) accords well with the experimental value (7.93 D).[5]

The lowest IP for untwisted compounds ($\omega = 0$) corresponds to ionisation from the highest delocalised π orbital. In (**4**) and (**5**) the aryl group is orthogonal to the double bond and it does not give any contribution to the π system. The reduction of IP values on going from (**2**) to (**9**) can be ascribed to the twist about the double bond rather than to a reduced electron-withdrawing ability of the acetyl with respect to that of cyano group. In fact, the ionisation potentials of the pairs of planar (or nearly planar) compounds (**1**), (**6**), and (**4**) and (**10**) are very similar.

The assignments previously suggested[6,7] for compounds (**2**) and (**9**) are confirmed by MNDO calculations, with a better quantitative agreement with respect to previous CNDO/2 results, as shown in Table 5. Equal splittings (0.47, 0.48 eV) between the 'lone pair' orbitals on the oxygen atoms are calculated for *ZZ* and *EZ* forms of compound (**9**), the antisymmetrical orbital $[n(0)_-]$ having higher energy than the symmetric one $[n(0)_+]$. IP of 9.2 eV (shoulder) of compound (**5**) is due to ionisation from the nearly degenerate orbitals of the benzene ring, orthogonal to the double bond.

The push–pull ethylenes considered in the present investigation can be split in three classes according to the relative magnitudes of E_π and E_S.

(a) E_π (90°) $\gg$ E_S (0°).—The energy minima fall at 0 (or nearly 0) and at 180° (or nearly 180°). Compounds (**1**), (**2**), (**4**)—(**6**), and (**10**) belong to this class. Their E_π values collected in Table 2 show that the lowering of the energy barrier on going from (**1**) to (**2**) and from (**4**) to (**5**) has to be ascribed to the increased ground-state steric energy. The acyl group lowers E_π more than cyano group does, as evidenced by comparing E_π (**4**) − E_π (**6**) = 15.8 kcal mol^{-1} with E_π (**4**) − E_π (**1**) = 9.8 and E_π (**10**) − E_π (**6**) = 10.2 kcal mol^{-1}. This finding is explained by MNDO calculations (Table 2) in terms of a reduced ground-state π-stabilisation by the acetyl group, which indicates a larger polarisation of the C=C bond than cyano and phenyl groups, rather than by charge-transfer effects in the transition states, which appear of comparable extent for the different substituents. The experimental barrier ($\Delta G^{\ddagger}$ 9.5 kcal mol^{-1}) of compound (**5**) is significantly overestimated by MNDO calculations (E_π 14.5 kcal mol^{-1}).

(b) E_π (90°) $\ll$ E_S (0°).—The molecules of this class, which includes systems (**3**) and (**9**), are markedly twisted about the C=C bond in the ground state. The predicted E_S for compound (**3**) amounts to 11.2 kcal mol^{-1}, and a higher value is expected for compound (**9**). The *EE* form of the latter resulted in the least stable structure, because of the strong dipole–dipole interactions. The *ZZ* form is predicted to be the most stable by MNDO calculation (Table 2), while low-temperature ^1H n.m.r. spectra of (**9**) were interpreted as a mixture of *EZ* and *ZZ* forms (ratio *ca.* 2:1) in deuteriochloroform solution.[10] Since increasing solvent polarity increases the population of the most polar conformer *EZ* at the expense of the symmetric *ZZ*, it appears reasonable that *ZZ* prevails in the gas phase.

The amount of splitting between the lone pair orbitals on the oxygen atoms observed by u.v. photoelectron spectra does not give any help for the choice of the dominating conformation as (see before) the splittings predicted by MNDO for *EZ* and *ZZ* forms are practically equal. The evaluation of the energy barrier related to the rotation of acetyl groups was possible by the dynamic n.m.r. technique, owing to the presence of a high E_S and the absence of E_π. As previously discussed, present MNDO calculations cannot predict the values of these barriers.

(c) E_π (90°) $\cong$ E_S (0°).—The minima fall near 45 and 135° twist angles. Compounds (**7**), (**8**), and (**11**) (Table 2) belong to this class. The *Z* form of (**7**) is markedly favoured over the *E* form; the E_π barrier is too low to be measured (3.7 kcal mol^{-1}) whereas the passage across the steric barrier (8.9 kcal mol^{-1}) could be detected on the n.m.r. time-scale. In (**8**), the *ZZ* form is more stable than the *EZ* form, as found also for methyl derivative (**9**). Both π and steric barriers are low (*ca.* 3—4 kcal mol^{-1}). The *Z* form of (**11**) is markedly favoured over the *E* form in line with the conclusions of the analysis of ^1H n.m.r. spectra. Appreciable maxima are predicted near 0 (E_S) and 90° (E_π).

On the whole, the present results give a clear indication of the role of theoretical calculations at MNDO level to rationalise static and dynamic experimental data related to the properties of the double bond of push–pull ethylenes. Reliable information on the most stable conformations and detailed descriptions of potential energy curves can be obtained, provided that a sufficient number of geometrical parameters are included in the energy-optimisation procedure.

In general MNDO calculations give a sound interpretation of ionisation potentials and dipole moments, and the quantitative agreement with experimental values is better than that obtained by previously adopted theoretical methods, at least in the case of the molecules studied in the present investigation. It appears also that theory can predict low energy barriers (< 5 kcal mol^{-1}) which cannot be detected by dynamic n.m.r., being out of the intrinsic time-scale of this spectroscopic technique. In this case reliable computational techniques could be safely used not only to predict very low conformational barriers, but also to plan new experiments.

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