An STO-3G Study of Acyclic 1,2-Ylides Derived from Iminium Ions

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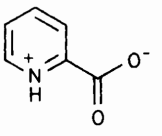
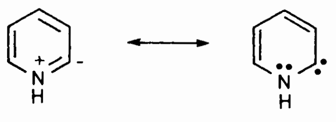
An STO-3G study of acyclic mono- and di-substituted 1,2-ylides derived from iminium ions has been carried out and these species are compared with the pyridinium and thiazolium ylides involved in the Hammick reaction and in processes involving the coenzyme thiamine pyrophosphate respectively. Calculated bond lengths, π-orbital populations and charges, indicate a variation of ylide and carbene character with substituent(s). For *C*-substituted iminium ylides, strong electron-attracting substituents promote the ylide form in preference to the carbene, whereas in *N*-substituted species, strong electron donors furnish the same effect. The thiazolium ylide, however, requires the inclusion of d orbitals or a 3-21G basis set at sulphur in the calculation to produce an acceptable geometry and electronic configuration. The lowest energy configuration of the acyclic carbene was found to be the singlet carbene. Barriers to rotation and inversion of an acyclic ylide were calculated and found to be comparable.

Hammick's early work on the thermal decarboxylation of pyridine-2-carboxylic acid[1,2] showed that decarboxylation occurred *via* the zwitterion (**1**) and produced a species, formulated as the 1,2-ylide (**2**), that could be trapped by aldehydes giving secondary alcohols (**4**). Subsequently the facile decarboxylation was ascribed to stabilisation of the 1,2-ylide by carbene resonance (**2**) ⟷ (**3**).[3]


(**1**)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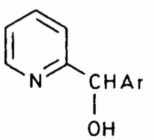
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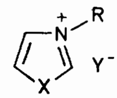
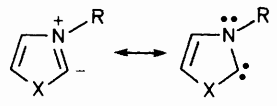
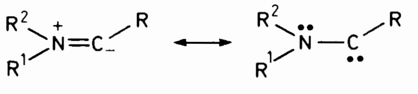
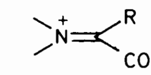

(**5**)**a**; X = S
b; X = O
c; X = NR


(**6**)**a**; X = S
b; X = O
c; X = NR
(**7**)

Breslow[4] and Westheimer[5] discovered a facile route to analogous thiazolium ylides involving deprotonation of thiazolium salts (**5a**). The ease of formation of the ylide (**6a**) is currently ascribed to the combined effect of the high s character of the C-2–H σ bond as shown by its unusually high ^{13}C–H coupling constant, the electron-withdrawing effect of the positively charged heterocycle, stabilisation of the ylide by carbene resonance (**6a**) ⟷ (**7a**), and overlap of the C-2 electron pair in (**6a**) with an empty d orbital on the adjacent sulphur atom.[6] That the latter effect is not crucial to the facile deprotonation of azolium salts is shown by the observation that the order of base-catalysed deuterium-exchange rates at C-2 is (**5b**) > (**5a**) > (**5c**).[6] The same rate order is observed for the decarboxylation of the zwitterionic azole-2-carboxylic acids.[7] Particular interest has been focussed on the thiazolium ylide (**6a**) because of its involvement in the biochemical processes, particularly α-keto acid decarboxylases and transketolases, mediated by the coenzyme thiamine pyrophosphate.[4,5,8] The widespread occurrence of histidine residues in proteins has likewise promoted interest in the imidazolium ylide (**6c**).[9] The 1,2-ylides (**2**) and (**6a–c**) have been found to react with a range of electrophiles.[10] Thus the moiety (**8**) ⟷ (**9**) possesses intrinsic stabilising features when part of an aromatic system in which R is a heteroatom or an sp^2 carbon centre, but it is unclear how much, if any, of this stabilisation derives from the incorporation of (**8**) ⟷ (**9**) into an aromatic ring.


(**8**) (**9**)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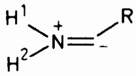
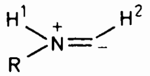

(**11**)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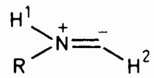
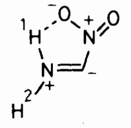

(**13**)


(**14**)

Discussion

Our interest in this area arises from our observation that acyclic examples of (**8**) ⟷ (**9**) can be generated by the facile decarboxylation of the analogous iminium carboxylates (**10**) and that the intermediate ylides can be trapped with elemental sulphur to give thioamides in good yield.[11] This encouraged us to carry out *ab initio* molecular-orbital calculations on various acyclic species (**11**)–(**13**) to probe the effect of substituents, and the geometry of the species, on (*a*) stability, and (*b*) the contribution of ylide (**8**) and carbene (**9**) to the overall structure of the species. For purposes of comparison, analogous

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Table 1. Total energies and stability order of monosubstituted ylides (**11**)–(**13**).

Substituent (R)	Total energy/hartrees (**11**)	(**12**)	(**13**)	$\Delta E_{(11-12)}$/ kcal mol^{-1}	$\Delta E_{(11-13)}$/ kcal mol^{-1}
H	−92.7446	—	—		
Me	−131.3537	−131.3460	−131.3467	4.83	4.39
CN	−183.3292	−183.2996	−183.3012	18.57	17.57
OMe	−205.3280	−205.1547	−205.1543	49.01	49.25
NMe_2	−224.2769	−224.1959	−224.1940	50.82	52.02
NO_2	−293.4991	−293.4539	−293.4569	28.36	24.78
Ph	−319.5272	−319.5229	−319.5217	2.7	3.45
p-$MeOC_6H_4$	−431.9472	−431.9360	−431.9345	7.03	7.98
p-$O_2NC_6H_4$	−520.2353	−520.2315	−520.2292	2.38	3.83
SMe	−524.5555	−524.5180	−524.5184	−23.54	−23.29

Table 2. HOMO and LUMO energies (eV) of monosubstituted ylides (**11**)–(**13**).

	HOMO			LUMO					
R	(**11**)	(**12**)	(**13**)	(**11**)	(**12**)	(**13**)	ΔE_{11}[a]	ΔE_{12}[a]	ΔE_{13}[a]
H	−0.2708	—	—	0.3198	—	—	0.5906	—	—
Me	−0.2562	−0.2659	−0.2636	0.3187	0.3338	0.3349	0.5749	0.5997	0.5985
CN	−0.3074	−0.3219	−0.3207	0.2126	0.2425	0.2628	0.52	0.5644	0.5835
OMe	−0.2719	−0.2818	−0.2762	0.3364	0.3162	0.3199	0.5537	0.598	0.5961
NMe_2	−0.2518	−0.2447	−0.2525	0.3685	0.3299	0.3313	0.6203	0.5746	0.5838
NO_2	−0.2943	−0.3066	−0.3144	0.1675	0.1691	0.1611	0.4618	0.4757	0.4755
Ph	−0.2511	−0.2611	−0.2686	0.2229	0.3184	0.2369	0.474	0.5795	0.5055
p-$MeOC_6H_4$	—	−0.2325	−0.2394	—	0.2503	0.2436	—	0.4828	0.483
p-$O_2NC_6H_4$	−0.2697	−0.2697	−0.2746	0.1526	0.3033	0.1542	0.4223	0.573	0.4288
SMe	−0.2552	−0.2545	−0.2531	0.3228	0.3300	0.3286	0.578	0.5845	0.5817

[a] HOMO-LUMO energy gap.

Table 3. STO-3G calculated geometries for (**11**).

	Bond lengths/Å				Bond angles/°		
R	R–C	C–N	N–H^2	N–H^1	RCN	CNH^2	CNH^1
H	1.120	1.339	1.023	1.026	103.7	120.1	126.8
Me	1.554	1.343	1.021	1.026	107.7	119.9	126.5
CN	1.494	1.337	1.023	1.026	108.9	118.9	126.8
OMe	1.374	1.364	1.017	1.023	104.2	119.9	124.1
NMe_2	1.377	1.367	1.016	1.019	113.5	117.7	128.2
NO_2	1.621	1.315	1.021	1.057	96.8	122.7	113.0
Ph	1.535	1.341	1.021	1.024	112.1	119.0	128.0
p-$MeOC_6H_4$	1.530	1.343	1.021	1.024	112.4	119.1	127.9
p-$O_2NC_6H_4$	1.541	1.339	1.021	1.024	111.9	118.8	128.1
SMe	1.765	1.351	1.021	1.025	108.3	119.4	126.9

calculations were also performed on some disubstituted acyclic ylides as well as (**2**), (**6a**, R = H), and (**6b**, R = H). Empirical structures were selected for calculation and all geometric variables optimised in each case with the exception of aromatic C–H bond lengths which were fixed at 1.08 Å and the torsion angles which were constrained to produce planar conformations.

Various semiempirical calculations have been reported on azolium cations and their ylides including extended Hückel and CNDO/2,[12] ARCANA,[13] and MNDO.[14] From calculations on the 1,3-dipole, $CH_2{=}\overset{+}{N}H{-}\overset{-}{O}$, it is clear that an unrestricted Hartree–Fock treatment (UHF) is sometimes necessary to completely represent biradical contributions (*e.g.* from $\dot{C}H_2{-}NH{-}\dot{O}$) although the difference in energy between UHF and restricted Hartree–Fock (RHF) treatments is only 6 kcal mol^{-1} at the 6-31G* level.[15,†] In other cases such as the dipole $HC{\equiv}\overset{+}{N}{-}\overset{-}{C}H_2$, there is no energy difference between the RHF and UHF calculations[15] and we have assumed that this is the case also for the species described here.

Total energies, HOMO and LUMO energies, and geometries for the monosubstituted species (**11**)–(**13**), derived from our RHF STO-3G calculations are collected in Tables 1–5. The possibility that dπ–pπ bonding might fulfil an important role in stabilising either thiazolium ylides or carbanions α to sulphur is the subject of contention[6,12,13,16a] with the consensus favouring no sulphur d-orbital participation. Thus the sulphur atom probably exerts its stabilising effect *via* polarisation of the C–S or N–S bonds (see below).

An analysis of the total energies shows that in all cases studied the *C*-substituted isomer (**11**) is more stable, by 2.3–50.8 kcal mol^{-1}, than either of the *N*-substituted isomers (**12**) and (**13**). The *C*-substituted isomer (**11**) is particularly favoured over (**12**) and (**13**) when heteroatoms (S,O,N) are directly attached to the

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† 1 cal = 4.18 J.

Table 4. STO-3G calculated geometries for (**12**).

	Bond lengths/Å				Bond angles/°		
R	R–N	C–N	N–H^1	CH^2	RNC	H^{1}NC	NCH^2
H	1.023	1.339	1.026	1.120	120.7	126.8	103.7
Me	1.476	1.338	1.028	1.114	122.3	124.5	103.6
CN	1.399	1.366	1.030	1.120	121.0	125.7	102.6
OMe	1.424	1.324	1.033	1.115	125.4	128.1	103.0
NMe_2	1.443	1.323	1.0313	1.115	123.5	126.9	103.0
NO_2	1.476	1.344	1.034	1.118	120.5	131.8	102.5
Ph	1.451	1.346	1.028	1.118	123.8	123.8	103.3
p-$MeOC_6H_4$	1.452	1.345	1.028	1.118	123.8	123.9	103.4
p-$O_2NC_6H_4$	1.445	1.350	1.028	1.118	123.3	124.1	103.3
SMe	1.749	1.329	1.030	1.118	125.80	123.9	103.8

Table 5. STO-3G calculated geometries for (**13**).

	Bond lengths/Å				Bond angles/°		
R	R–N	C–N	N–H^1	C–H^2	RNC	H^{1}NC	NCH^2
H	1.0258	1.339	1.0227	1.1198	126.8	120.1	103.7
Me	1.4802	1.3378	1.0256	1.1192	129.5	117.6	103.9
CN	1.4005	1.3653	1.0271	1.1194	127.3	118.8	103.8
OMe	1.4327	1.326	1.0307	1.1175	123.8	121.8	103.6
NMe_2	1.4516	1.3214	1.0283	1.1133	132.7	118.8	105.9
NO_2	1.4892	1.3394	1.0305	1.1193	126.2	125.4	103.6
Ph	1.4569	1.3453	1.0257	1.1163	132.3	116.3	104.9
p-$MeOC_6H_4$	1.4587	1.3439	1.0257	1.1163	132.3	116.3	104.9
p-$O_2NC_6H_4$	1.452	1.3498	1.0256	1.1162	132.1	116.3	104.9
SMe	1.7583	1.3296	1.028	1.1194	128.8	117.3	104.7

Table 6. Calculated π-orbital populations,[a] charges,[b] and C–N bond lengths in (**11**).

R	C	qN^π	d_{C-N}/Å
H	0.3151	+0.3151	1.339
Me	0.3168	+0.2960	1.343
CN	0.3708	+0.3415	1.337
OMe	0.4166	+0.2504	1.364
NMe_2	0.4409	+0.2153	1.367
NO_2	0.4262	+0.4203	1.315
Ph	0.3494	+0.3014	1.341
p-$MeOC_6H_4$	0.3505	+0.2962	1.343
p-$O_2NC_6H_4$	0.3523	+0.3132	1.339
SMe	0.3908	+0.2727	1.351

[a] C is the calculated electron population of the π-orbital on carbon. [b] qN^π is the nominal charge at nitrogen obtained by subtracting the actual π-electron population from that present in the π-orbital of atomic nitrogen in the same configuration.

Table 7. Calculated π-orbital populations,[a] charges,[b] and C–N bond lengths in (**12**).[a]

R	N	qC^π	d_{C-N}/Å
H	1.6849	−0.3151	1.339
Me	1.6547	−0.3338	1.338
CN	1.6770	−0.2617	1.366
OMe	1.6394	−0.3816	1.324
NMe_2	1.6287	−0.4008	1.323
NO_2	1.6780	−0.2814	1.344
Ph	1.6390	−0.3184	1.346
p-$MeOC_6H_4$	1.6375	−0.3243	1.345
p-$O_2NC_6H_4$	1.6435	−0.3033	1.350
SMe	1.6460	−0.3699	1.329

[a] N is the calculated electron population of the π-orbital on nitrogen. [b] qC^π is the nominal π-charge at carbon obtained by subtracting the actual π-electron population from that present in the π-orbital on atomic carbon in the same electronic configuration.

ylidic carbon atom (Table 1) with NMe_2 (50.8) > OMe (49.0) > SMe (23.6 k cal). Electron-withdrawing groups directly attached to ylidic carbon also exert substantial stabilising effects with NO_2 > CN, whilst aryl substitution has a much smaller effect. In all cases the aryl substituents are almost coplanar with the rest of the molecular framework. In the *N*-substituted isomers (**12**) and (**13**), heteroatom and aryl substituents favour the *Z*-isomer (**12**) whilst the electronegative substituents, CN and NO_2, favour the *E*-isomer (**13**).

The presence of electron-withdrawing substituents (CN, NO_2) results in the lowest HOMO energies, in accord with the expected ionisation potentials of these compounds where the electrons are more firmly bound (Table 2). The converse is expected and found for electron-donor groups such as NMe_2 and SMe (Table 2). In contrast, the LUMO energies reflect the electron affinities of each structure and those containing electron-withdrawing groups would be expected to have lower energies than those possessing donor groups which is in accord with the calculated results. Tables 3–5 summarise the calculated bond lengths and bond angles for (**11**)–(**13**). The calculated RCN bond angle for (**11**, R = NO_2) is unusually small and the CNH^1 bond angle somewhat larger than those of other members of the series. These atypical angles may reflect intramolecular hydrogen bonding between the nitro substituent and H^1 as in (**14**). This is supported by the acidity of the *cis*-hydrogen atom, the increased length of the N–O bond involved in the interaction, *i.e.* 1.29 compared with 1.25 Å for the other oxygen atom, and the O–H internuclear distance (*ca.* 1.8 Å).

Data on gross orbital populations and C–N bond lengths for (**11**)–(**13**) are collected in Tables 6–8. For the *C*-substituted ylide

(**11**) there is a net transfer of electrons from the π-orbital of nitrogen (which contains 2 electrons in the parent nitrogen molecule in the same sp^2 electronic configuration) to that on carbon. This transfer reflects the ylide ⟷ carbene contribution to the overall structure with the ylide represented as the species which has one electron in each of the π orbitals of carbon and nitrogen, and the carbene containing both electrons as a lone pair on nitrogen with the carbon π-orbital vacant. As expected, π-donors in (**11**) reduce the π-donation from nitrogen to carbon in the order $NMe_2 > MeO > MeS$, whilst π acceptors enhance the effect in the order $NO_2 > CN$. This effect is accompanied by a shortening of the C–N bond for electron-withdrawing groups due to greater overlap between the π-orbitals and the reverse for electron-donor substituents (see below). In the *N*-substituted ylides (**12**) and (**13**), π donors attached to the nitrogen atom increase the electron transfer to carbon, whilst π acceptors show the opposite trend with $CN > NO_2 >$ aryl.

Table 8. Calculated π-orbital populations,[a] charges,[b] and C–N bond lengths in (13).[a]

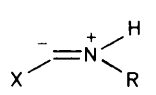
R	N	qC^{π}	$d_{C-N(R)}$/Å
H	1.6849	−0.3151	1.229
Me	1.6539	−0.3350	1.338
CN	1.6745	−0.2628	1.365
OMe	1.6505	−0.3495	1.329
NMe_2	1.6257	−0.4037	1.321
NO_2	1.6745	−0.2853	1.339
C_6H_5	1.6354	−0.3265	1.344
p-$O_2NC_6H_4$	1.6419	−0.3049	1.345
SMe	1.6582	−0.3418	1.326

[a] See Table 7 for definitions.

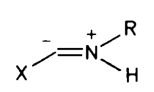
Table 9. Energies and gross π-orbital charges for disubstituted and cyclic ylides.[a]

Compound	Total energy/ hartrees	qC^{π}	qN^{π}
(**15a**)	−405.8651	−0.4273	+0.3885
(**16a**)	−405.8792	−0.4589	+0.4324
(**15b**)	−405.9191	−0.4162	+0.2574
(**16b**)	−405.9212	−0.3958	+0.2551
(**2**)	−243.5567	−0.4282	+0.4209
(**6a**)	−560.4823	−1.9900	+0.1503
(**6a**)[b]	−560.8837	−0.4300	+0.4900
(**6b**)	−241.4711	−0.5000	+0.3466

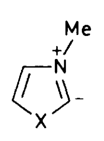
[a] For definitions of qC^{π} and qN^{π} see Tables 6 and 7. [b] Calculated structure with an extended basis set at the 3-21G level.



(**15**)a; X = NO_2, R = OMe
b; X = OMe, R = NO_2



(**16**)a; X = NO_2, R = OMe
b; X = OMe, R = NO_2



(**17**)a; X = S
b; X = O

STO-3G calculations were also performed on a number of disubstituted ylides (**15**) and (**16**) and on (**2**), (**6a**), and (**6b**) for comparison purposes (Tables 9 and 10).

The results obtained for the cyclic ylide (**6a**) at the STO-3G level are clearly inaccurate with predicted bond angles of 77.8 for C–S–C and 98.8° for C–N–C. Furthermore, the calculated Mulliken population analysis shows that the lone pair of electrons located at the ylidic carbon which normally lies in the molecular plane, now lies perpendicular to the ring plane. It is concluded that a minimal basis set is inadequate for representation of the properties of sulphur in these systems, and accordingly, a further series of calculations have been carried out incorporating either 'd' functions (scaling factor = 1) or a 3-21G basis set at the sulphur atom. Both of these options give a substantially better result with C–S–C angles of 97.7 for the former and 93.1° for the latter. The expected electronic configuration is also reproduced with the ylidic lone pair now lying in the molecular plane in both cases. Compared with their acyclic analogues both (**2**) and the azolium ylides (**6a**) and (**6b**) show an increase in qN^{π} (Table 9).

Ylide Carbene Resonance.—A comparison between the calculated data for (**11**) and (**12**) shows that the species with a π-donor substituent on the nitrogen atom, *e.g.* (**12**; R = NMe_2) or a π-acceptor on the carbon atom, *e.g.* (**11**, R = NO_2) exhibit the largest electron accumulation in the ylidic carbon π orbital with consequent increase in ylide character (**8**). In contrast, species which exhibit the largest carbene character (**9**) are those with the smallest electron accumulation in the ylidic carbon π-orbital as in (**11**; R = NMe_2) and (**12**; R = NO_2 or CN). For the *C*-substituted ylides (**11**) there is a noticeable increase in C–N bond length with $NMe_2 \approx OMe > SMe$ which reflects the resonance interaction of these substituents, *e.g.* (**18**) ⟷ (**19**) rather than increased carbene character. In all cases the trivalent nitrogen atom is sp^2 hybridised and the NO_2 group is coplanar with the ylide framework. Using values of 1.28 and 1.41 Å for the C=N and C–N bond lengths respectively* it can

Table 10. Geometries of disubstituted and cyclic ylides.

	Bond lengths/Å				Bond angles/°		
Compound	X–C	C–N	N–R	N–H	XCN	CNR	CNH
(**15a**)	1.557	1.328	1.430	1.03[a]	110.2	129.3	115.5
(**16a**)	1.610	1.319	1.417	1.03[a]	96.4	121.3	114.6
(**15b**)	1.346	1.392	1.465	1.03[a]	107.7	131.6	119.9
(**16b**)	1.355	1.394	1.449	1.03[a]	103.0	120.6	128.4
(**2**)	1.474	1.376	1.402	1.026	108.6	128.9	116.5
(**6a**)	1.788	1.477	1.401	1.012	125.7	129.6	131.6
(**6a**)[b]	1.677	1.382	1.416	1.025	104.3	118.3	121.4
(**17a**)[c]	1.696	1.362	1.436	—	108.7	114.7	—
(**6b**)	1.369	1.380	1.421	1.021	102.4	123.8	123.6
(**17**)[c]	1.335	1.402	1.414	—	106.1	109.2	—

[a] Not optimised. [b] Calculated structure with an extended basis set at the 3-21G level. [c] Data for (**17a**) and (**17b**) taken from MNDO calculations reported in ref. 14.

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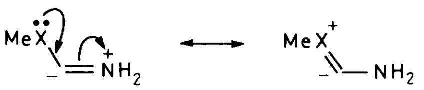
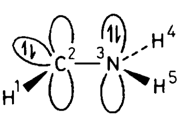
* Average values derived from the Cambridge Crystallographic Database.[16b]

be seen from Tables 6–8 that substantial contributions to the overall electronic structure are made by both the ylide and carbene canonical forms. The carbon–nitrogen bond lengths in Tables 6–8 range from 1.32–1.37 Å with an average value of 1.34 Å.

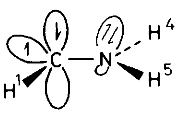


(18) X = NMe, O, or S **(19)**

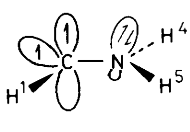
With the exception of thiazolium ylide (**6a**) the cyclic ylides are predicted to be far less stable than the disubstituted ylides (**15a, b**) and (**16a, b**) (Table 9). The three cyclic ylides (**2**), (**6a**), and (**6b**) show a similar contribution from their respective carbene canonical forms as the acyclic analogues as evidenced by the calculated C–N bond lengths (Table 9). The high qC^{π} and low qN^{π} values resulting from STO-3G calculations suggest carbene (**7a**) makes a very large contribution to the overall structure of (**6a**). This result is closer to earlier crude calculations[17] based on the π-approximation method than to recent MNDO calculations which suggest that the contribution of (**7c**) is 50%.[14] However, repeating the calculations with d orbitals or an extended basis set on sulphur (Table 9) gives results indicating the contribution of carbene (**7a**) to the overall structure of (**6a**) is in the range 43–52% depending on the method of calculation. In the disubstituted acyclic ylides the electronic push–pull effects of the methoxy- and nitro-substituents do not have a major perturbing effect on the gross π-orbital charge and C–N bond lengths compared with the monosubstituted species (compare Tables 6–8 with Tables 9–10). The most noticeable change occurs for (**16b**) which shows an increased contribution from the carbene canonical form.



(20)



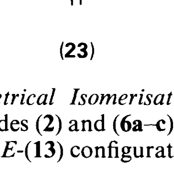
(21)



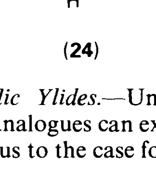
(22)

There are three possible electronic configurations (**20**)–(**22**) for the parent carbene and the relative energies and conformations of these were explored by STO-3G calculations with full geometry optimisation. The relative energies were found to lie in the order (**20**) < (**22**) < (**21**), with (**20**) more stable than (**22**) by *ca.* 5 kcal mol^{-1} whilst (**21**) lies *ca.* 57 kcal mol^{-1} above (**20**). The STO-3G method is however not reliable for (**22**).

The calculated minimum-energy conformations are best expressed in terms of the H–H torsion angles. For (**20**) the calculated H^1–H^5 and H^1–H^4 torsion angles are 0 and 180° respectively whilst for (**21**) the H^1–H^5 torsion angle is 89.6° and the H^1–H^4 torsion angle is 150.7°. This latter conformation is depicted in (**23**) whilst for (**22**) the lowest energy conformation is (**24**) with the H^1–H^4 and H^1–H^5 torsion angles both 121.7°.

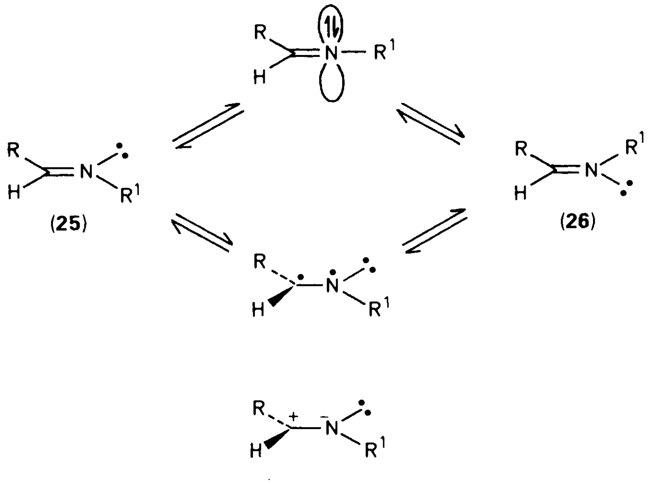


(23)



(24)

Geometrical Isomerisation of Acyclic Ylides.—Unlike the cyclic ylides (**2**) and (**6a–c**), the acyclic analogues can exist in *Z*-(**12**) and *E*-(**13**) configurations analogous to the case for imines (**25**) and (**26**). Two major uncatalysed mechanisms have been considered for the direct interconversion of (**25**) and (**26**).[18,19] One involves passage of the lone pair through the plane of the imine framework (Scheme), whilst the other involves rotation about the C=N bond generating an orthogonal diradical or charge-separated species. A third facile, indirect mechanism involving imine–enamine tautomerism, is well established but requires R in (**25**) and (**26**) to possess a labile hydrogen α to C=N moiety,[20] and processes involving *N*-protonation, but not enamine formation, are well established.[21]



Scheme.

For simple imines the inversion barrier is appreciably smaller than the rotation barrier [≥30 kcal mol^{-1} for methyleneimine (**25**; R = R^1 = H)].[18] However, in imidate anions HCONR (R = H or alkyl) rotation about the C–N bond is favoured over nitrogen inversion, albeit by a small amount (≤6 kcal mol^{-1}).[19]

We have calculated the barriers to inversion and rotation for the parent acyclic ylide (**11**; R = H) using STO-3G. The inversion barrier was calculated by varying the NCH^2 angle in (**12**; R = H) from 90 to 180° in 15° increments with all other geometric variables optimised. The rotation barrier was calculated by constraining the molecule to be planar apart from the H^2CNH^1 torsion angle which was varied from 0 to 180° in increments of 15°. The barrier heights of both processes are rather similar, with the barrier to rotation (57.6 kcal mol^{-1}) slightly lower than the barrier to inversion (61.2 kcal mol^{-1}).

Calculations.—Most calculations reported here were carried out on a DEC Vax 8600 series computer except those on structures such as (**6a**) at the 3-21G level, and some phenyl derivatives of (**11**), (**12**), and (**13**) at the STO-3G level, which were both CPU intensive and required large amounts of storage for integrals. In these cases, an IBM 3090 series computer was used with up to a gigabyte of storage available for the two electron integrals. All calculations were carried out with the GAMESS *ab initio* method using the usual *z*-matrix input of geometric variables to give final geometries which were characterised as minima *via* the Hessian matrix in the normal way.[22]

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Paper 9/00424F
Received 26*th January* 1989
Accepted 18*th May* 1989