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STUDIES OF POLARIZED ETHYLENES—XI[a]

CONFORMATIONAL ANALYSIS AND BARRIERS TO ROTATION OF THE ELECTRON-ACCEPTING GROUPS IN TWISTED PUSH–PULL ETHYLENES

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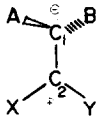
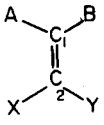
Abstract—A number of 1,1-diacetylethylenes with electron-donating groups on C_2 has been studied, in which steric interactions between the acetyl groups and the donor groups lead to a permanent twist around the formal C–C double bond. This twist enhances the charge separation and gives the Ac–C–Ac part a carbanion-like character. The rotation of the acetyl groups is hindered, with free energy barriers in the range 12.3–13.7 kcal mol^{-1}, and of their three possible arrangements, EE, EZ and ZZ, only the latter two are observed. The degenerate EZ–ZE topomerization is found to go with the ZZ but at least in one case also with the EE form as intermediate.

In one 1-phenyl-1-acetyl analogue the barrier to rotation of the acetyl group is increased to 16.7 kcal mol^{-1}. The rotation of 1-aryl groups is also hindered, and the relation of the barrier to this rotation to steric factors has been studied in two 1-p-nitrophenyl-1-cyanoethylenes.

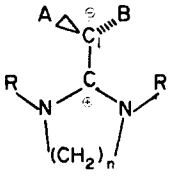
Ethylenes with electron-accepting substituents on one C atom (C_1) and electron-donating substituents on the other (C_2) are polarized with the excess negative charge on C_1 and its substituents.[1] If there is also a strong steric interaction between the donor and acceptor groups, the molecules may be permanently twisted about the double bond.[2,3] In such distorted molecules the overlap between the p orbitals on C_1 and C_2 will be diminished, and the π electrons from the formal double bond will be partly localized in the electron-accepting part, which will have a carbanion-like structure, whereas a partial positive charge will be localized in the carbonium ion-like donor part. Thus Ia is a better representation of these molecules than Ib.



Ia



Ib



II

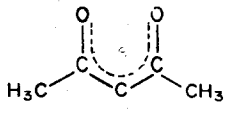
In planar push–pull ethylenes (Ib) the conjugation across the double bond leads to hindered rotation of the donor and acceptor groups with sometimes quite high barriers.[4,5] In the twisted analogues (Ia) the increased negative charge should lead to still higher barriers to rotation of the acceptor groups.

In previous communications[2,3] it was shown that twisted push–pull ethylenes can be obtained by using two alkylamino groups connected by an ethylene or trimethylene bridge as donor groups (II, n = 2 or 3). In compounds of type Ib with dimethylamino groups as donors the steric strain is relieved by a rotation of these groups out of the plane of the C_2–N bonds, whereas in II the semi-rigid cyclic structure prevents this and leads to a twist around the formal double bond. As could be expected, the steric effect and thus the angle of twist is larger with a six-membered than with a five-membered ring. The twist angle can also be modified by variation of the size of the N-alkyl groups.

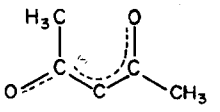
Previously, the barriers to rotation about the formal double bond ("steric" and "π-electronic" barriers) were examined,[2,3] and we now wish to report results from a study of the conformations and rotational barriers of some acceptor substituents in the electron-rich part of the molecule. From an electronic point of view this part is an approximation of a carbanion, and the rotational barriers of the acceptor groups should provide lower limits to the corresponding barriers in free carbanions. The compounds included in this study are shown in Scheme 1.

RESULTS AND DISCUSSION

The 1,1-*diacetylethylenes* **1–7**. There has been a considerable interest in the conformations of enolates derived from β-diketones (III). Much of the work has been concentrated on the influence of metal ions on the enolate structure and its dependence on concentration, solvent, and temperature.[6,7]



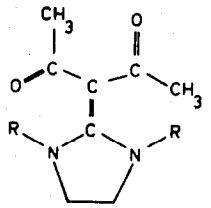
ZZ–III



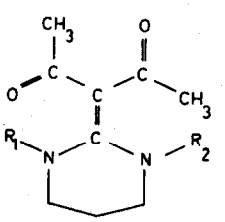
EZ–III

The strong cation-anion interactions in these systems make it difficult to assess the conformational preference of the "free" anion, but Noe and Raban[8] have shown that the ZZ form of the acetylacetonate ion (III) with parallel C–O groups, is favoured by chelation but that

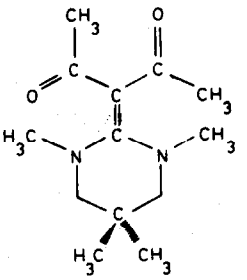
[a]Part X. C. Dreier, L. Henrihsen, S. Karlsson and J. Sandström, *Acta Chem. Scand.* B32, 281 (1978).



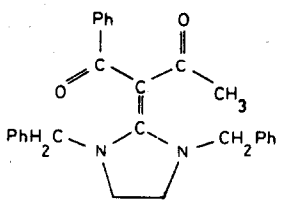
1. R = CH_3
4. R = CH_2Ph



2. $R_1 = R_2 = CH_3$
5. $R_1 = R_2 = CH_2Ph$
6. $R_1 = R_2 = iPr$
7. $R_1 = iPr$, $R_2 = CH_2Ph$



3



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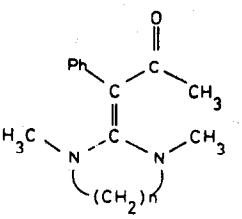
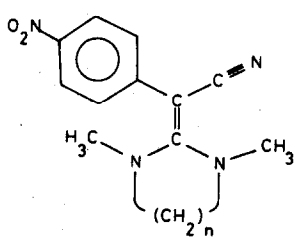
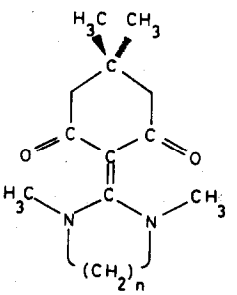


9. n = 2
10. n = 3



11. n = 2
12. n = 3

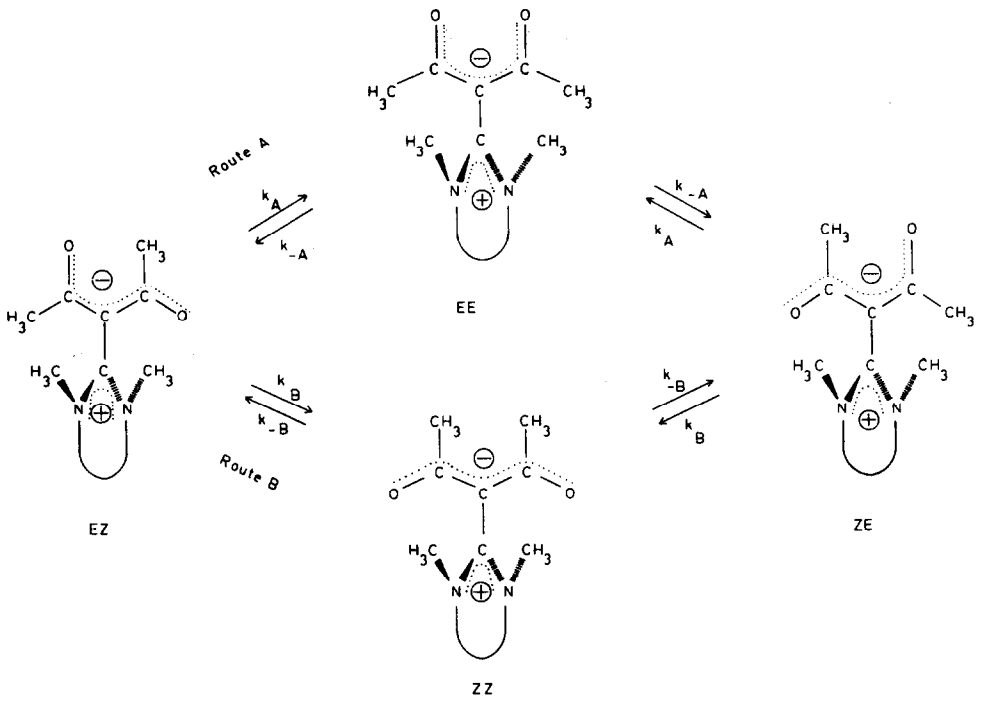


13. n = 2
14. n = 3

Scheme 1. The compounds used in this study.

complexation of the cation with crown ether leads to an increase in the population of the EZ form. This latter is probably the dominating conformation of the free anion, where the ZZ form is destabilized by dipole–dipole repulsion. 1,1-Diacetylethylenes like 1–7 in Scheme 1 have the same conformational possibilities with respect to the acetyl groups as III (Scheme 2, note that the E and Z designations have to be exchanged when going from III to 1–7[9]). Therefore 1–7 are of interest as analogues of β-diketone anions free from interactions with chelating metal ions.

The ^1H spectrum of 1 in dichlorofluoromethane at ambient temperature displays three sharp singlets, one due to the ring methylene protons at δ 3.76, one for the N–Me groups at δ 2.91 and one for the acetyl Me groups at δ 2.19. At −67° the rotation of the acetyl groups is slow on the NMR timescale, and the N–Me resonance has split into two signals at δ 2.98 and δ 2.86 with the intensity ratio close to 2:1. The acetyl Me resonance now appears as three signals of approximately equal intensity at δ 2.45, δ 2.39 and δ 1.80. The ring methylene protons give two broad signals of unequal intensity, and they have not been considered further. To understand these splittings it is necessary to have an appreciation of the rate of passage of the C_1Ac_2 group through the plane of the imidazolidine ring and through the 90° twisted state. An acceptable model for 1 which permits an estimate of these rates is 8, which has acceptor groups of fairly similar capacity and also rather similar steric interactions. A complete bandshape study of 8[2] gave $\Delta H^{\neq}$ = 19.2 kcal mol^{-1} and $\Delta S^{\neq} = +7.7$ e.u. for the passage through the planar state, whereas the passage through the 90° twisted state was found to be fast at −130°. For passage through the planar state rate constants of



Scheme 2. Exchange diagram for 1,1-diacetylethylenes 1–7.

10^{-1} s^{-1} at 0° and 2×10^{-7} at −67° can be calculated, and similar values probably also apply to 1. Thus, the acetyl Me groups should be equivalent in the EE and in the ZZ forms, but non-equivalent in the EZ (ZE) form. The N-Me signals should be equivalent in the EE and in the ZZ forms, and because of the fast passage through the 90° twisted state they should be isochronous in the EZ (ZE) form as well. The spectrum observed at −67° indicated the presence of the EZ form and only one of the symmetrical EE and ZZ forms.

The same general behaviour is shown by all compounds 1–7, though with varying population ratios. The high-field and the low-field acetyl Me signals always have the same intensity and can thus be assigned to the EZ form.

The least stable of the two symmetrical forms should be EE because of the dipole–dipole repulsion, and it seems likely that the observed form is ZZ. This assignment is supported by the aromatic solvent induced shift (ASIS, Fig. 1). Aromatic solvent molecules tend to solvate preferentially the positive region of dipolar molecules and to avoid the negative regions.[10,11] In several analogues of 1 the protons in the imidazolidine ring have been found to be those most strongly shielded by an aromatic solvent, whereas the N-alkyl protons are less shielded, and the protons on the acceptor part are deshielded.[5] If a model of 1 is placed in the anisotropic magnetic field of aromatic rings[12] as shown in Fig. 2, the experimental order of shielding and deshielding is well reproduced. The Me protons of the E acetyl group fall in a strongly deshielding and those of the Z acetyl group in a weakly deshielding region, as the methylene protons in the rigid models 13 and 14 (Fig. 1). The acetyl Me protons of the symmetrical forms of 1 and 2 are only weakly deshielded, whereas one of these groups in the EZ form is strongly and the other weakly deshielded, which all is in agreement with the symmetrical form having the ZZ conformation.

Increasing solvent polarity should increase the population of the more polar rotamer, the order of dipole moments being ZZ < EZ < EE.[1] On dilution of a deuteriochloroform (D = 4.7, E_T = 39.1)[13] solution of 1 with pyridine (D = 12.3, E_T = 40.2),[13] the population of the EZ form increases at the expense of the symmetric form, in agreement with the above assignment.

It is worth observing that the E acetyl proton resonance falls at lower field than that of the Z group (Table 1), though the opposite should have been expected considering the normal anisotropy of the CO groups.

The analogue of 1 with two dimethylamino groups as donor groups also shows hindered rotation of the acetyl groups, but here only the EZ form is observed.[5] No good explanation for this difference can be given at present.

The ZZ:EZ ratio in compounds 1–7 varies from 0.2 in 6 to 1.5 in 5, but no simple relation between this ratio and the ring size or the substituents on the nitrogen atoms has been found.

The exchange between the EZ and ZE forms (Scheme 2) can take place with the EE or ZZ forms as intermediates, the direct route with simultaneous rotation of the acetyl groups certainly having too high activation energy to be feasible. Since the N-alkyl groups are equivalent in each of the two observed rotamers, their ^1H resonances present a two site exchange system EZ (ZE)⇌ZZ with the rate constants k_B and $2k_{-B}$. Their bandshapes are not affected by a possible exchange between EZ and ZE via route A. The acetyl proton resonances, on the other hand, exchange between three sites, EZ(E), EZ(Z) and ZZ, and from their bandshapes it is in principle possible to obtain more detailed mechanistic information.

The rate constants k_B and k_{-B} for 1 were evaluated from the N-Me resonances; and they were used to simulate the acetyl proton resonances. It was found that insertion of $k_A = 0.1\,k_B$ improved the fit between experimental and calculated bandshapes, indicating that

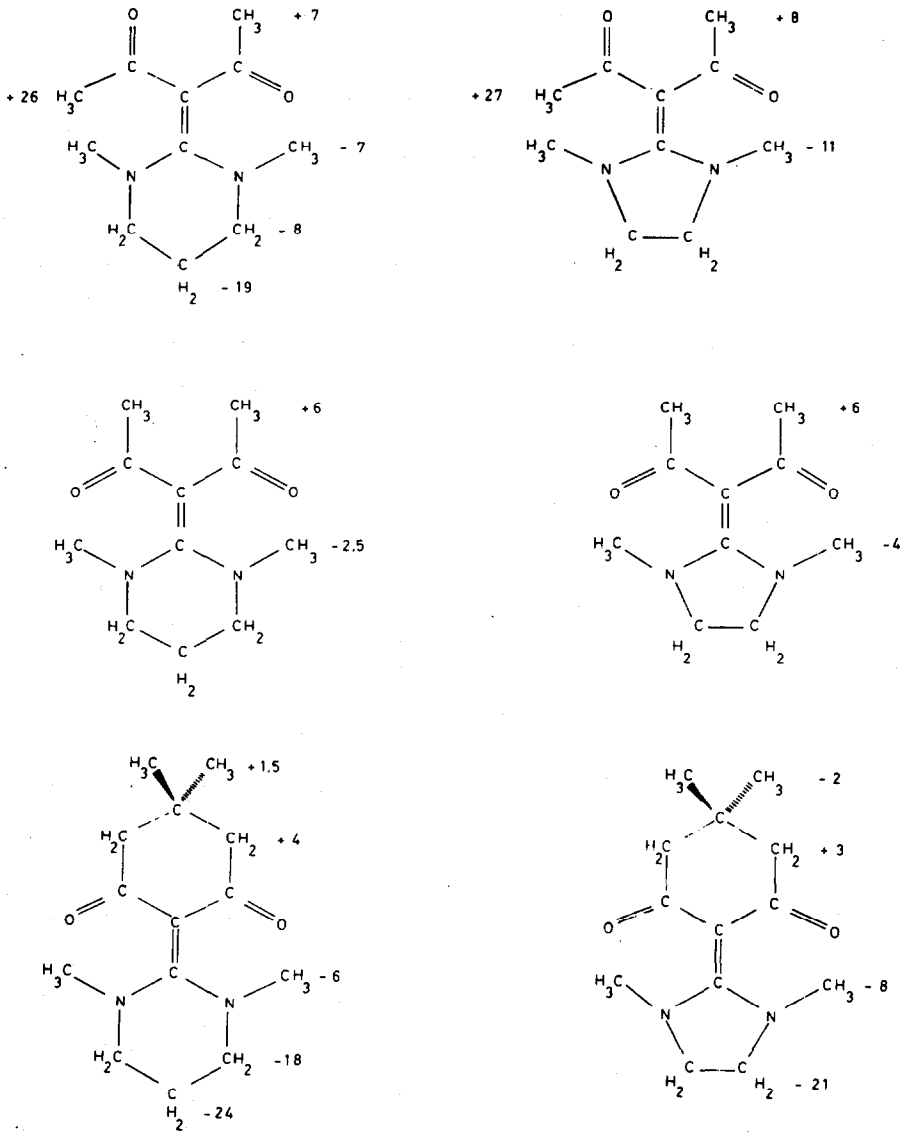


Fig. 1. ASIS shifts (see experimental part) in compounds **1**, **2**, **13** and **14**.

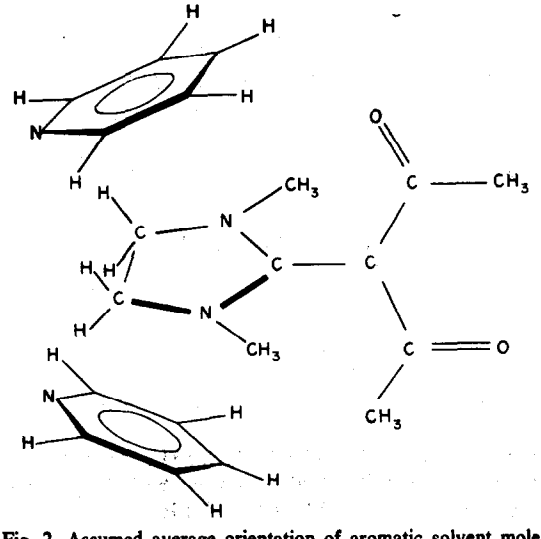


Fig. 2. Assumed average orientation of aromatic solvent molecules around compounds of type **1**.

the EE form plays some role as intermediate in spite of its high energy. However, due to temperature dependent chemical shifts and the uncertainty in the T_2 determinations, this ratio of rate constants is on the borderline of the experimental accuracy, and the conclusion must be viewed with caution. The free energy barrier to the EZ→ZZ exchange was found to be 12.3 kcal mol^{-1} at −40° (Table 2).

Analysis of the N-Me resonances in **2** gave a value of 13.4 kcal mol^{-1} for the corresponding barrier. The explanation for the higher barrier in the 6-membered ring compound may be found in a larger C_1–C_2 twist angle with a concomitant larger negative charge on the Ac–C_1–Ac part of the molecule. Furthermore, the larger ring introduces a greater steric strain both in the initial state and in the transition state, but a model shows that the interaction is stronger in the transition state, and the net result must be an increase in $\Delta G^{\neq}$.

Unfortunately, the quintuplet from the central ring methylene group overlaps the acetyl resonances, and an accurate analysis of the three site exchange system was not possible. Instead, **3** was synthesized, in which the

Table 1. Chemical shifts[a] and rotamer populations for the 1,1-diacetylethylenes 1–7.

		EZ				ZZ		
Compound	Temp K	δ_{N-R}	δ_{CCH_3} (E)	δ_{CCH_3} (Z)	p[b]	δ_{N-R}	δ_{CCH_3}	p
1	206	2.98	2.45	1.80	0.67	2.86	2.39	0.33
2	195	3.16	2.41	1.81	0.73	3.05	2.33	0.27
3	208	3.17	2.44	1.85	0.58	3.05	2.36	0.42
4	210	4.50	2.58	1.99	0.50	4.43	2.46	0.50
5	217	4.77	2.51	1.98	0.40	4.69	2.37	0.60
6	217	4.70[c]	2.46	1.84	0.83	4.61[c]	2.36	0.17
7	217	–	2.48	1.87	0.68	–	2.37	0.32

[a] In ppm, downfield from TMS in solvent $CHCl_2F$.
[b] Fractional population.
[c] For the benzylic methylene protons.

Table 2. Free energy barriers for the acetyl rotations in the 1,1-diacetylethylenes 1–5

Compound	Temp K	$\Delta G^{\ddagger}_{EZ \rightarrow ZZ}$ kcal mol^{-1}	$\Delta G^{\ddagger}_{EZ \rightarrow EE}$ kcal mol^{-1}
1	233.9	12.30	
	237.3	12.37	(13.8)
	240.5	12.34	(13.4)
2	224.1	13.25	
	237.9	13.36	
	249.7	13.53	
3	246.8	13.55	13.83
	257.8	13.74	14.15
	291.1	14.01	14.41
4	229.3	12.33	
	239.0	12.35	
	247.8	12.37	
5	250.6	13.54	
	258.2	13.55	
	277.1	13.69	

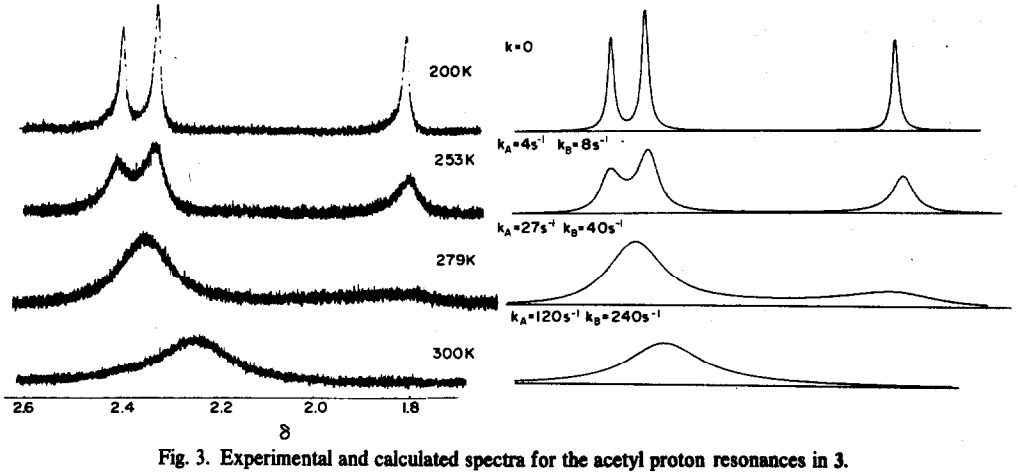


Fig. 3. Experimental and calculated spectra for the acetyl proton resonances in 3.

two disturbing protons have been replaced by Me groups. In this compound, the N–CH_3 and N–CH_2 resonances overlapped, and estimation of k_B from the bandshape of the N-Me resonance was not possible. In the acetyl exchange system, however, it was necessary to include $k_A = 0.5\,k_B$ to obtain a good fit (Fig. 3). Thus in this case there is no doubt that the EZ⇌ZE exchange proceeds with both the ZZ and EE forms as intermediates.

In 6 and 7 overlapping resonances precluded meaning-

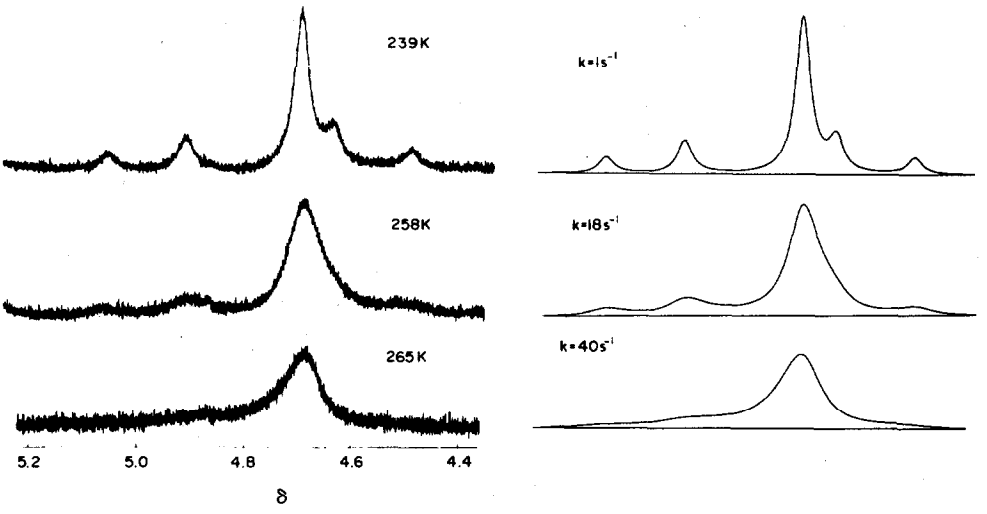


Fig. 4. Experimental and calculated spectra for the benzylic methylene proton resonances in **5**.

ful barrier determinations, but in **4** and **5** the benzylic methylene protons serve as a useful probe for the exchange. At temperatures below −40° they give an AB pattern for the EZ conformation and a singlet for the ZZ conformation. The AB spectrum, which constitutes a further proof for the permanent twist at the C_1–C_2 bond, is affected by exchange both by routes A and B as distinct from the N-Me resonances of **1**, **2** and **3**, which are only affected by route B. In the simulation of the exchange-broadened spectra, no significant exchange by route A had to be assumed (Fig. 4). The free activation energy for the EZ→ZZ exchange (route B) was found to be 12.4 kcal mol^{-1} for **4** and 13.6 kcal mol^{-1} for **5**.

A comparison of the barriers for **1** and **4** and for **2** and **5** (Table 2) show that the steric effect of a benzyl group is not significantly different from that of a Me group at the same temperature. In the cyclohexane series a small but significant difference between the A values for these substituents has been observed.[14]

It is worth noticing that the barrier to acetyl group rotation (EZ→ZZ) in sodium acetylacetonate is 12.9± 0.2 kcal mol^{-1} in pyridine solution,[8] i.e. it falls between the barriers for the 5- and 6-membered diacetyl compounds **1–5**. A crude approach could lead to the conclusion that the C_1–C_2 bond is a pure single bond in **1–7** and that a full negative charge is delocalized on the Ac–C_1–Ac part to make it equivalent with the anion. However, as discussed above, the acetyl group rotation in **1–7** involves a steric interference with the donor part which raises the barrier, and it is at present not possible to estimate the magnitude of this contribution.

The 1-*acetyl*-1-*phenylethylenes* **9** *and* **10**. In these compounds one acetyl group has been replaced by a less electron-demanding phenyl group. Consequently, the excess electrons on the acceptor part will to a greater extent be localized in the remaining acetyl group and increase its barrier to rotation.

In the ^{1}H NMR spectrum of **9** at −40° the C–CH_3, N–CH_3 and N–CH_2 signals appear as doublets in the ratio 96 : 4, with the N–CH_2 signal broadened due to slow rotation about the C_1–C_2 bond. The population ratio is unfavourable for bandshape analysis, but the rate constant for the acetyl group rotation was evaluated by monitoring the ratio of the intensities of the major N–CH_3 and C–CH_3 signals to that of the Me resonance of added dimethyl phthalate. The temperatures at which these ratios had their minimum values could be found with reasonable accuracy. By simulating the spectra the rate constants which minimized the $I_{N\text{–}CH_3}/I_{ref}$ and I_{CCH_3}/I_{ref} ratios were found. Thus a free energy barrier of 11.5 ± 0.2 kcal mol^{-1} could be found for the major→minor exchange at −12°.

On dilution of a deuteriochloroform solution of **9** with pyridine, the population of the minor rotamer increased, and it is therefore assigned to the E conformation. The ASIS effects were small and inconclusive.

In the spectrum of **10** both the acetyl and N-Me resonances appear as doublets at ambient temperature with the intensity ratio 0.32 : 0.68. The more intense signals were assigned to the E form by their increase in intensity and by the larger downfield shift of the acetyl Me signal on dilution of a deuteriochloroform solution with pyridine. The free energy barrier to the Z→E exchange was found to be 16.7 kcal mol^{-1} at 33°.

The explanation for the higher barrier to acetyl rotation in **10** than in **9** may be found in the same effects as were discussed for **1** and **2**, namely: (1) The twist angle θ and therefore also the partial negative charge on Ac_2C_1 is larger in the 6-membered compound, and (2) the steric interaction between the acetyl group and the N-Me group in the transition state to acetyl rotation is also stronger in **2** and **10** than in **1** and **9**. However, the difference between the acetyl rotational barriers in **1** and **2** is only *ca.* 1 kcal mol^{-1}, whereas it is *ca.* 5 kcal mol^{-1} between **9** and **10**. Part of the reason for this may be found in differences in the π-electron contribution to the C_1–C_2 torosional barrier. This barrier is roughly described by (1), where V^{steric} has a maximum for $\theta = 0$ and falls off rapidly with increasing θ. It may safely be assumed that V_0^{π} is larger for **9** and **10** than for **1** and **2**.

$$V^{tors} = V^{steric} + V^{\pi} = V^{steric} + 0.5\, V_0^{\pi}[1 + \cos 2(\theta + \pi/2)]. \quad (1)$$

This assumption is based on the free energy barriers toward C_1–C_2 rotation (π-barriers) for the 2,2-bis(dimethylamino) analogues, which are 9.3 kcal mol^{-1} for the analogue of **9** and <8.0 kcal mol^{-1} for the analogue of **1**.[5] The difference in V_0^{π} is probably augmented in the transition state to acetyl rotation since then one

Table 3. Barriers to rotation of the acceptor groups in 9–12

Compound	Group	Solvent	Temp K	Δν Hz	$\Delta G^{\ddagger}$ kcal mol^{-1}
9	Ac (Z → E)	$CHCl_2F$	306	5.8	16.7
10	Ac (Z → E)	$CDCl_3$	261	13.5	11.5
11	p-$NO_2C_6H_4$	CH_2Cl_2	174	56.3	8.3
12	p-$NO_2C_6H_4$	CH_2Cl_2	260	60.0	12.6

acetyl group is turned out of conjugation, and the remaining acetyl group in **1**, **2** is a much better acceptor than the phenyl group in **9**, **10**. It is probable that the increased steric strain in the transition state to acetyl rotation leads to an increase in θ ($\Delta\theta$), and that $\Delta\theta$ is larger in **2** and **10** than in **1** and **9**. Provided that $\Delta\theta$ is similar in **1** and **9** and in **2** and **10**, which is a reasonable assumption, the contribution from V^{π} to the acetyl rotational barrier will increase more when going from **9** to **10** than from **1** to **2**.

The 1-*cyano*-1-p-*nitrophenylethylenes* **11** *and* **12**. Hindered rotation of aryl groups has been observed in 1-aryl-1-cyano-2,2-bisdimethylaminoethylenes, and the free energy barrier to rotation of a *p*-nitrophenyl group in this system has been reported as 10.9[4] and 11.6[5] kcal mol^{-1}. The rates of rotation were evaluated by an approximate method, treating the high-field part of the aromatic protons as a superposition of two exchanging doublets. and using the coalescence approximation, discussed in Ref. 15. That such a treatment is permissible has been demonstrated in a similar case[16] by comparison with spectra calculated by DNMR-3.[17]

For **11** a coalescence was observed at −99°, giving a free energy barrier of 8.3 kcal mol^{-1} (Table 2). The corresponding barrier for **12** was found to be 12.6 kcal mol^{-1} at −13°. The difference between these two barriers can probably be explained in the same way as that between **9** and **10**.

The effect of C_1–C_2 twist on uv spectra of push–pull ethylenes has been studied by Wennerbeck,[18] who used the 2,2-bisdimethylamino compounds as untwisted and 5-membered cyclic analogues as twisted models. It was observed that twisting in most cases was accompanied by a shift of the absorption maximum toward that of the anion of the active methylene compound corresponding to the acceptor part of the molecule, the donor part (approaching an amidinium ion structure) having no strong absorption in the near uv or visible region. The absorption spectra of **11** and **12** fit well into this picture, with λ_{max} for the bisdimethylamino compound equal to 418 nm (ϵ = 22,000), for **11** 435 nm (ϵ = 22,800), for **12** 450 nm (ϵ = 24,700), and for tetrabutylammonium *p*-nitrophenylcyanomethanide 596 nm (ϵ = 4800). The large difference between **12** and the anion shows that the C_1–C_2 twist angle is still far from 90° in the ethylenes, though some twisting of the *p*-nitrophenyl ring out of the NC–C_1–C_{ar} plane is probably also involved.

EXPERIMENTAL

NMR spectra. All ^{1}H NMR spectra were recorded on a JEOL Model JNM-MH 100 NMR spectrometer, equipped with a standard variable temp. controller (VT 3-c). The temps. were measured by monitoring the voltage of the internal thermocouple with a sensitive digital voltmeter. The thermocouple readings were calibrated after each experiment with an external copper–constantan thermocouple placed at the height of the receiver coil in a dummy tube containing 0.5 ml of acetone. The samples for low-temp. spectra were *ca.* 0.8 M in $CHCl_2F$ with TMS added to provide an internal lock signal. They were thoroughly degassed by repeated freeze-thaw cycles under high vacuum before being sealed off.

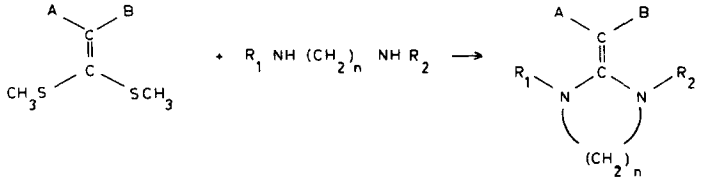
The rate constants were evaluated by visual fitting of the experimental spectra to spectra calculated by the McConnell expression[19] for simple 2-site cases, by solving three simultaneous Block equations for the simple 3-site cases, and by the DNMR-3 program[17] on a 3-site case with couplings in two sites for the benzylic methylene protons in **4** and **5**. The determination of T_2 was performed by the usual method,[16] using one of the solvent signals as a resolution standard.

The ASIS values given in Fig. 1 are the changes in chemical shift (in Hz, positive for downfield shift) from a $CHCl_2F$ or $CDCl_3$ soln to a soln in $CDCl_3$-pyridine (1:1, v/v). This mixture had to be used since the compounds are insufficiently soluble in pure aromatic solvents.

Preparative part. All compounds were prepared by reaction between the appropriate 2,2-bismethylthioethylene and N,N'-substituted diamine (Scheme 3). The preparation of **2** is described as an example.

1,3-Dimethyl-2-(pentane-2,4-dion-3-ylidene) hexahydropyridine (**2**). N,N'-Dimetyl-1,3-diaminopropane (1.0 g, 0.1 mol) was added to a soln of 1,1-diacetyl-2,2-bismethylthioethylene[20] (2.0 g, 0.01 mol) in dry toluene (25 ml). The mixture was refluxed for 1 hr, and on cooling the pure product crystallized in 95% yield, m.p. 217–219°. (Found: C 62.8, H 8.69, N 13.2. $C_{11}H_{18}N_2O_2$ requires: C 62.8, H 8.63, N 13.3%).

For the following compounds solvent for recrystallization, yield, and m.p. are given in this order.



Scheme 3. General method of synthesis.

1,3,5,5 - Tetramethyl - 2 - (pentane - 2,4 - dion - 3 - ylidene) hexahydropyrimidine (3). Xylene-cyclohexane (1:1), 60%, 162–164°. (Found: C 64.7, H9.49, N11.6. $C_{13}H_{22}N_2O_2$ requires: C 65.5, H 9.30, N 11.7%).

1,3-*Dibenzyl-2-(pentane-2,4-dion-3-yliden) imidazolidine* (4). Xylene, 61%, 140–143° (Found: C 75.5, H 7.04, N 8.09, O 9.25. $C_{22}H_{24}N_2O_2$ requires: C 75.8, H 6.85, N 8.04, O 9.19%).

1,3 - *Dibenzyl* - 2 - (*pentane* - 2,4 - *dion* - 3 - *ylidene*) *hexahydropyrimidine* (5). Xylene, 66%, 167–168°. (Found: C 76.6, H 7.53, N 7.76. $C_{23}H_{26}N_2O_2$ requires: C 76.2, H 7.26, N 7.73%).

1,3 - *Diisopropyl* - 2 - (*pentane* - 2,4 - *dion* - 3 - *ylidene* - *hexahydropyrimidine* (6). Xylene, 38%, 196–197°. (Found: C 68.4, H 9.99, N 10.6. $C_{15}H_{26}N_2O_2$ requires: C 67.6, H 9.84, N 10.5%).

1 - *Benzyl* - 3 - *isopropyl* - 2 - (*pentane* - 2,4 - *dion* - 3 - *ylidene*) *hexahydropyrimidine* (7). Xylene, 85%, 165–167°. (Found: C 72.7, H 8.38, N 8.87. $C_{19}H_{26}N_2O_2$ requires: C 72.6, H 8.33, N 8.91%).

1,3 - *Dimethyl* - 2 - (1 - *phenylpropan* - 2 - *on* - 1 - *ylidene*) *hexahydropyrimidine* (10). Benzene-ligroin (4:1), 30%, 63–65°.

1,3 - *Dimethyl* - 2 - (α - *cyano* - p - *nitrobenzylidene*) *hexahydropyrimidine* (12). Xylene, 70%, 211–213°. (Found: C 61.9, H 5.74, N 20.7. $C_{14}H_{16}N_4O_2$ requires: C 61.8, H 5.92, N 20.6%).

1,3 - *Dimethyl* - 2(5,5 - *dimethylcyclohexane* - 1,3 - *dion* - 2 - *yliden*) *imidazolidine* (13). Toulene, 83%, 224–225°. (Found: C 66.1, H 8.51, N 11.8. $C_{13}H_{20}B_2O_2$ requires: C 66.1, H 8.53, N 11.85%). The preparation of the intermediate ketene mercaptal is described in Ref. 2.

1,3 - *Dimethyl* - 2 - (5,5 - *dimethylcyclohexane* - 1,3 - *dion* - 2 - *ylidene*) *hexahydropyrimidine* (14). Xylene, 43%, 212–214°. The preparation of 1, 8 and 9 is described in Ref. 21.

N,N',2,2-tetramethyl-1,3-diaminopropane used in the preparation of 3 was prepared by methylation of 2,3-dimethyl-1,3-diaminopropane[22] via the diformyl derivative as described for analogous diamines in Ref. 2. The crude product was used directly in the synthesis of 3.

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