Conformational Aspects of Substituents in Enamines. X-Ray Structure Analyses and Quantum Chemical Calculations *

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Z. Naturforsch. **47 a,** 869–876 (1992); received March 18, 1992

Dedicated to Professor Dr. Hermann Stetter on the Occasion of his 75th Birthday

X-ray structure determination of the enamine (*Z*)-4-(6′-t-butoxycarbonyl-2′,2′-dimethyl-5′-phenyl-3′-hexen-3′-yl)morpholine (**1**) reveals that certain bulky groups may enforce a relative orientation of the molecular subunits without conjugative interaction between the nitrogen lone pair and the olefinic double bond. According to the results of quantum chemical ab initio calculations the experimentally found arrangement would be the least favourable one in the absence of such substituents. A careful analysis of the molecular structure of **1** shows that this unusual arrangement is due to the presence of both, the α- and the β-substituent.

In (*E*)-4-(3′-t-butoxycarbonylmethyl-1′-phenyl-1′-penten-1′-yl)morpholine (**2**) rather the nitrogen lone pair than the phenyl π system is in conjugation with the olefinic double bound. The results of ab initio calculations on model compounds show that conjugation of the double bond with the nitrogen lone pair is by 2–6 kcal/mol more favourable than conjugative interaction between the phenyl group and the C=C bond. Closer examination of the molecular structure of **2**, however, led to the conclusion that it is predominantly the β-substituent which forces the phenyl ring in a position where conjugation with the enamine double bond is not possible.

1. Introduction

Recently we reported on the role of β-lithiated enamines as enolate equivalents in Michael additions to enoates [1]. In that communication we stressed the experimental aspects of our work and only briefly discussed the results of X-ray structure determinations of two enaminoesters, (*Z*)-4-(6′-t-butoxycarbonyl-2′,2′-dimethyl-5′-phenyl-3′-hexen-3′-yl)-morpholine (**1**) and (*E*)-4-(3′-t-butoxycarbonylmethyl-1′-phenyl-1′-penten-1′-yl)morpholine (**2**). We now discuss these structures in more detail and complement our experimental data with the results of quantum chemical calculations performed in order to estimate the influence of substituents on the relative orientation of the nitrogen lone pair and the olefinic double bond.

2. Computational Methods

The structures were solved by means of direct methods as implemented in the XTAL 2.6 system of crystallographic programs [2], employing GENSIN [3] to generate structure invariant relationships and GENTAN [4] for the general tangent phasing procedure.

While all crystallographic and semiempirical calculations were performed on a local VAX workstation 3100, the quantum chemical ab initio calculations were carried out on the IBM 3900 computer system of the *Rechenzentrum der Rheinisch-Westfälischen Technischen Hochschule Aachen.*

All quantum chemical ab initio calculations [a] were performed employing the GAMESS program package [5], while we used the MOPAC program [6] for semiempirical calculations with the MNDO [7], MINDO/3 [8], and AM1 [9] method. Starting from reasonable geometries defined by means of standard geometrical parameters we optimized sets of cartesian coordinates for some model compounds with the MNDO method [b]. The resulting data sets served as starting points for further refinement on the one determinant HF-SCF level of ab initio theory, employing the split valence 3-21G [10] and 6-31G [11] basis sets. If not indicated otherwise the structures have completely been optimized. To get more reliable relative energies we calculated in some cases correlation corrections by means of second order Møller-Plesset perturbation theory [12] (MP2/6-31G//6-31G).

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* Presented in part at the 27th Symposium on Theoretical Chemistry, September 1–5, 1991, Lage-Hörste, FRG.

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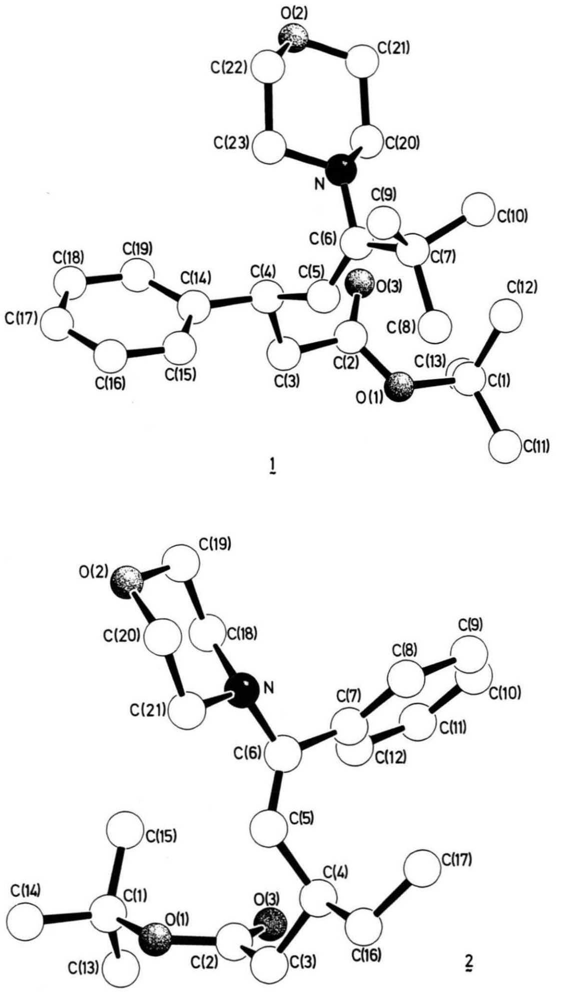


Fig. 1. a) Solid state structure of **1**. b) Solid state structure of **2**.

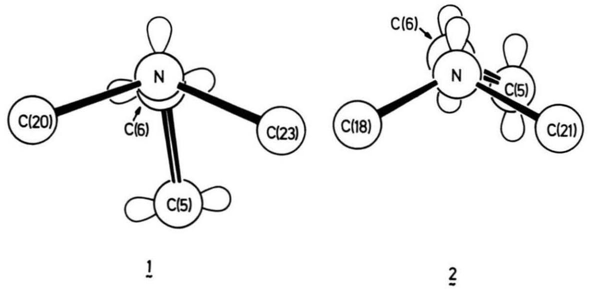


Fig. 2. Relative orientation of the olefinic double bond and the next neighbours of the nitrogen atom in the morpholine substituent in **1** and **2**.

Table 1. Crystal structure determination of **1** and **2** [f].

	1	**2**
Formula	$C_{23}H_{35}O_3N$	$C_{21}H_{31}O_3N$
M_r	373.54	345.49
$D_{cal}/g \cdot cm^{-3}$	1.093	1.107
T/K	293	293
Crystal system	triclinic	monoclinic
Space group (No.)	$P\bar{1}$(2)	$P2_1/n$ (14)
Z	2	4
a/Å	8.671(3)	10.004(2)
b/Å	12.078(6)	13.926(2)
c/Å	12.156(6)	14.890(4)
α/deg.	112.73(2)	
β/deg.	90.65(3)	92.78(1)
γ/deg.	103.33(2)	
V/Å^3	1135.39	2072.02
Reflection for cell constants (range)	25 ($9.51 \leq \theta \leq 19.57$)	25 ($10.10 \leq \theta \leq 16.60$)
$F(000)$	408	752
λ/Å	0.71069	0.71069
μ (MoK$_\alpha$)/cm^{-1}	0.66	0.68
r^* (Zachariasen coefficient)	$0.22 \cdot 10^4$	$0.60 \cdot 10^4$
Scan	$\Omega/2\theta$	$\Omega/2\theta$
$(\sin \theta/\lambda)_{max}$ [c]	0.6	0.6
Total number of reflections	6101 ($\pm h \pm k + l$)	5378 ($\pm h + k + l$)
Obserbed reflections $I > 2\sigma(I)$	3270	2400
Variables	245	227
$R(Rw)$	0.075 (0.065)	0.064 (0.060)
$\Delta\varrho$/e · Å^{-3}	0.3	0.3
Diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4

In addition we performed partial geometry optimizations on **1** and **2** with the MNDO method starting from the solid state structures.

3. Results and Discussion

3.1. Structures of 1 and 2 in the Solid State

SCHAKAL [13] plots of **1** and **2** are given in Figures 1a and 1b. The drawings in Figure 2 show the relative orientations of the olefinic double bonds and the next neighbours of the nitrogen atom in the morpholino-groups. Technical details of the structure determinations are given in Table 1. The fractional atomic coordinates of non-hydrogen atoms of **1** and **2** are listed in Tables 2 and 3.

1 and **2** are formally similar in that their amine part is morpholine and that they carry bulky substituents in both the α- and the β-position of the olefinic double bond. They differ, however, as far as spatial demands and relative orientation of the substituents are concerned. For instance, while the α-substituent of **1** is a sphere-like t-butyl group, it is a flat phenyl ring in **2**. Moreover, the configuration of **1** is *Z*, while the configuration of the C=C bond is *E* in **2**.

The steric demands of the α-substituents are also reflected by the wide C(4)–C(5)–C(6) angles, which are 129.8(2)° in **1** and 128.0(3)° in **2**. The spatial needs of the t-butyl groups result in wide C(1)–O(1)–C(2) angles of about 121°, while the corresponding values in some methyl esters are 115–117° [14].

As expected, in both compounds the morpholino-groups have a chair conformation with the olefinic system in an equatorial position. The nitrogen atoms of both molecules are clearly pyramidalized with no clear indication of flattening in **2** as a result of the interaction between the nitrogen lone pair and the neighbouring double bond. With sums of bond angles at the nitrogen atom of 344.5° in **1** and 343.6° in **2**, we obtain a pyramidalization [15] of 49.2% in **1** while the corresponding value is 52.1% in **2**.

The carbon atom C(6) and its nearest neighbours are essentially coplanar in both molecules.

As far as the relative orientation of the nitrogen lone pair and the π system of the C=C double bond are concerned, **1** is an atypical enamine.

Whereas in most vinylamines with known structures [16] like **2** the nitrogen lone pair and the 2p orbitals of the olefinic segment are more or less parallel to each other, they are virtually orthogonal in the case of **1**. With dihedral angles of C(23)–N–C(6)–C(5) = −56.9(4)° and C(23)–N–C(6)–C(7) = 118.9(3)° the plane defined by the atoms C(5), C(6), and C(7) almost bisects the angle enclosed by C(23), N, and C(20), resulting in a minimal π-conjugative interaction between the olefinic part and the nitrogen lone pair. As a result, at 1.451(3) Å the exocyclic C–N bond in **1** is longer than in those cases where such an interaction is possible. So, e.g., the corresponding bond length is 1.423(4) Å in **2**. This is still relatively long but nevertheless typical for an usual enamine with its nitrogen atom involved in a morpholino-system [16]. Although the difference between these bond lengths in **1** and **2** is not too large, it qualitatively parallels not only our computational results (vide infra) but also the experimental findings of other authors [17]. In this regard it is of interest to compare the different types of exocyclic C–N bonds in 1,1,2-trimorpholinoethene [17], where the nitrogen atoms of

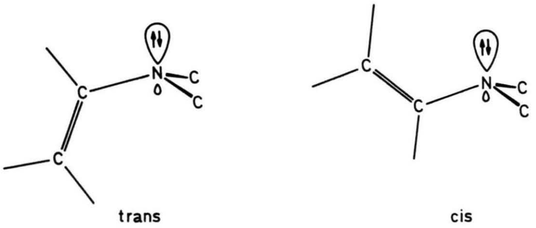
Table 2. Non-hydrogen atom coordinates and equivalent isotropic thermal parameters of **1**.

	x/a	y/b	z/c	U_{eq} [h]
O(1)	0.4423(2)	0.1965(2)	0.5810(2)	0.052(1)
O(2)	−0.3359(2)	0.0775(2)	0.7831(2)	0.082(1)
O(3)	0.1795(2)	0.1280(2)	0.5195(2)	0.074(1)
N	−0.0055(2)	0.1580(2)	0.8537(2)	0.045(1)
C(1)	0.4602(4)	0.3106(3)	0.5604(3)	0.057(2)
C(2)	0.3002(4)	0.1150(3)	0.5584(3)	0.050(1)
C(3)	0.3050(3)	0.0064(2)	0.5871(3)	0.047(1)
C(4)	0.1919(3)	−0.0026(2)	0.6821(2)	0.041(1)
C(5)	0.2486(3)	0.1098(2)	0.7971(2)	0.043(1)
C(6)	0.1668(3)	0.1818(2)	0.8704(2)	0.042(1)
C(7)	0.2406(3)	0.2931(3)	0.9862(3)	0.053(1)
C(8)	0.4242(4)	0.3263(3)	0.9970(3)	0.076(2)
C(9)	0.1872(4)	0.2635(3)	1.0918(3)	0.084(2)
C(10)	0.1910(4)	0.4077(3)	0.9929(3)	0.081(2)
C(11)	0.6363(4)	0.3732(3)	0.5977(4)	0.092(2)
C(12)	0.3616(4)	0.3904(3)	0.6398(3)	0.081(2)
C(13)	0.4194(4)	0.2797(3)	0.4305(3)	0.081(2)
C(14)	0.1758(3)	−0.1243(2)	0.6944(2)	0.043(1)
C(15)	0.2755(4)	−0.1390(3)	0.7748(3)	0.062(2)
C(16)	0.2564(5)	−0.2530(4)	0.7807(3)	0.080(2)
C(17)	0.1397(5)	−0.3523(3)	0.7098(4)	0.084(2)
C(18)	0.0399(4)	−0.3393(3)	0.6313(4)	0.077(2)
C(19)	0.0583(4)	−0.2277(3)	0.6221(3)	0.060(2)
C(20)	−0.0728(3)	0.1898(3)	0.7635(3)	0.058(2)
C(21)	−0.2454(4)	0.1918(3)	0.7854(3)	0.076(2)
C(22)	−0.2681(4)	0.0464(3)	0.8683(3)	0.074(2)
C(23)	−0.0970(3)	0.0389(3)	0.8476(3)	0.057(2)

Table 3. Non-hydrogen atom coordinates and equivalent isotropic thermal parameters of **2**.

	x/a	y/b	z/c	U_{eq} [h]
O(1)	0.4422(2)	−0.0430(2)	0.3510(1)	0.056(1)
O(2)	0.1266(2)	1.1879(2)	0.9799(2)	0.069(2)
O(3)	0.5875(2)	0.8873(2)	0.6848(2)	0.083(2)
N	0.1873(3)	1.0235(2)	0.8770(2)	0.049(2)
C(1)	0.3200(4)	−0.0761(3)	0.3014(2)	0.061(2)
C(2)	0.5227(3)	0.9498(3)	0.6479(2)	0.058(2)
C(3)	0.3904(3)	0.9344(2)	0.5980(2)	0.056(2)
C(4)	0.2852(3)	0.8975(2)	0.6604(2)	0.049(2)
C(5)	0.2544(3)	0.9700(2)	0.7309(2)	0.051(2)
C(6)	0.2442(3)	0.9559(2)	0.8183(2)	0.047(2)
C(7)	0.2790(3)	0.8626(2)	0.8644(2)	0.046(2)
C(8)	0.1813(3)	0.8128(2)	0.9068(2)	0.063(2)
C(9)	0.2104(4)	0.7250(3)	0.9477(3)	0.077(3)
C(10)	0.3353(5)	0.6893(3)	0.9484(3)	0.076(3)
C(11)	0.4331(4)	0.7380(3)	0.9075(3)	0.075(3)
C(12)	0.4064(3)	0.8254(2)	0.8657(2)	0.060(2)
C(13)	0.2002(4)	−0.0299(3)	0.3407(3)	0.095(3)
C(14)	0.3205(4)	−0.1834(3)	0.3196(3)	0.081(3)
C(15)	0.3344(5)	−0.0592(3)	0.2040(3)	0.101(3)
C(16)	0.1584(3)	0.8679(3)	0.6061(2)	0.062(2)
C(17)	0.0562(3)	0.8172(3)	0.6606(2)	0.072(2)
C(18)	0.2685(3)	1.0501(2)	0.9571(2)	0.060(2)
C(19)	0.1862(4)	1.1053(3)	1.0201(2)	0.070(2)
C(20)	0.0461(4)	1.1599(2)	0.9032(3)	0.066(2)
C(21)	0.1259(3)	1.1088(2)	0.8353(2)	0.056(2)

the two geminal morpholino-substituents are oriented in such a way that their lone pairs can partly overlap with the π system of the double bond, while this overlap is much smaller for the third substituent. Accordingly, for this substituent the exocyclic C–N bond is slightly longer (1.442(4) Å) than those linking the two geminal morpholino-groups to the C=C segment (1.415(4) and 1.398(4) Å [17]), while it is not too different from the corresponding bond length in **1**. Different from **1**, however, in this case the nitrogen lone pair of the non-interacting morpholino system and the C=C double bond are almost oriented cis to each other (cf. Scheme 1).



Scheme 1

In both, **1** and **2**, the length of the C(5)=C(6) bond (1.324(4) Å in **1** and 1.325(4) Å in **2**) is that of a typical olefinic double bond (1.319–1.334 [18]). In general, the length of this bond seems to be relatively insensitive to conjugation with an adjacent nitrogen lone pair [16].

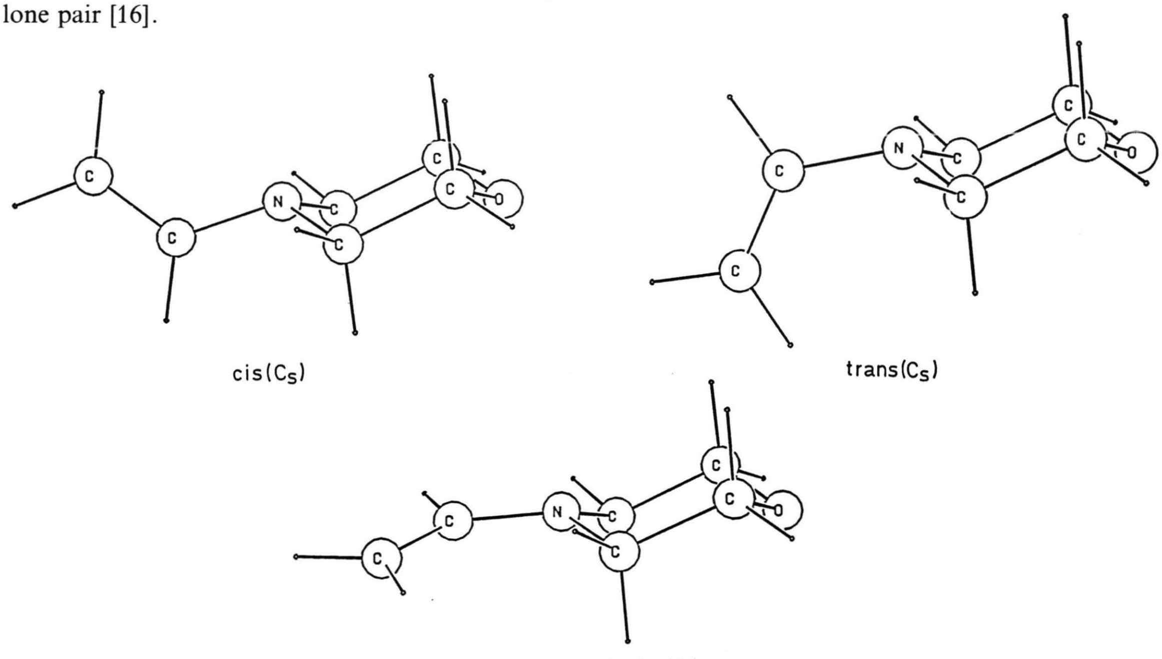
Table 4. Total energies (in a.u.) of cis-, trans-, and fully optimized 4-vinylmorpholine. The values in parentheses are energies relative to the most stable species (in kcal/mol) [g].

	cis	Fully optimized	trans
3-21G//3-21G	–360.858141 (4.6)	–360.865398 (0.0)	–360.855529 (6.2)
6-31G//6-31G	–362.709374 (5.3)	–362.717748 (0.0)	–362.706228 (7.2)
MP2/6-31G//6-31G	–363.466542 (5.1)	–363.474639 (0.0)	–363.463209 (7.2)

3.2. Calculations

Total and relative ab initio energies of our model compounds are given in Table 4. Plots of the cis- and trans-conformers (which have been optimized under constraint of C_s symmetry) and of fully optimized 4-vinylmorpholine are given in Fig. 3 (for numbering of atoms in the calculations see Scheme 2).

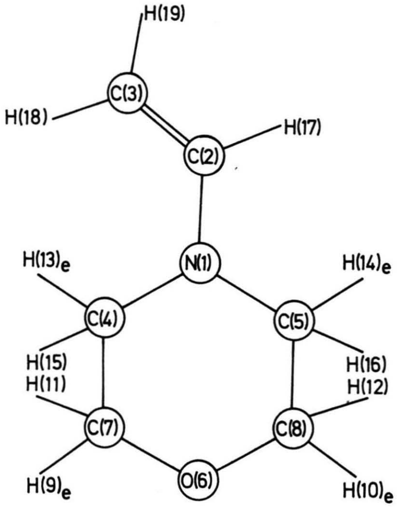
Since ab initio calculations with reasonable basis sets for compounds with bulky substituents like **1** and **2** are not feasible at the moment, we confined our ab initio studies to the height of the barrier towards rotation about the C–N bond in 4-vinylmorpholine and the relative energies of the corresponding cis- and trans conformers. At all levels of accuracy the cis



cis(C_s) trans(C_s)

without constraint (C_1)

Fig. 3. Structures of cis-, trans-, and fully optimized 4-vinylmorpholine obtained with the 6-31G basis set.



Scheme 2. Numbering of atoms in the ab initio calculations. The subscript "e" indicates hydrogen atoms in equatorial positions.

conformer is about 5 kcal/mol higher in energy than the fully optimized species. With the 3-21G basis set the trans conformer was found to be by 6.2 kcal/mol less stable than the fully optimized structure. This energy difference is increased to 7.2 kcal/mol at the 6-31G//6-31G level, and inclusion of Møller-Plesset corrections to the second order (MP2/6-31G//6-31G) does not further alter this value.

With the 6-31G** basis set Sevin et al. [19] obtained an energy difference of 10.1 kcal/mol between the completely optimized and the trans conformer of vinylamine. However, for the trans form they used the fully optimized bond lengths and angles of the planar compound and constrained the corresponding dihedral angle to 90°. Reoptimization of vinylamine in a fixed trans conformation will reduce this energy gap, probably to a value not too different from the one obtained for 4-vinylmorpholine. Thus, employing the approximate but nonempirical PRDDO method, Müller et al. [20] found the cis- and trans conformers of vinylamine to be by 7.1 and 7.9 kcal/mol higher in energy than the completely optimized structure^{d}.

Facing the small energy difference between the cis- and the trans isomer it is not surprising that the relative orientation of the olefinic double bond and the nitrogen lone pair in **1** is not cis, although this conformation is somewhat lower in energy than the trans form in the case of unsubstituted 4-vinylmorpholine. Obviously the repulsive interaction between the methyl groups of the t-butyl substituent and the hydrogens at C(20) and C(23) (cf. Fig. 4a and c) of the morpholino system which is stronger in the cis- than in the trans conformer is sufficient to surmount this small energy difference. In the completely optimized species (6-31G//6-31G) the dihedral angle C(4)–N(1)–C(2)–C(3) is 3.8° (cf. Fig. 3 and Scheme 2). Thus, the interaction between the olefinic π system and the nitrogen lone pair is possible. This is not only reflected by a relatively short C(2)–N(1) bond of 1.390 Å, but also by a small increase of the C(2)=C(3) bond length (1.330 vs. 1.321 Å in ethene). With 1.320 Å and 1.323 Å in the cis- and the trans conformer the lengths of these bonds are close to the value for free ethene, while the lengths of the C(2)–N(1) bonds are 1.428 Å (cis) and 1.432 Å (trans), respectively.

We performed additional semiempirical MNDO calculations in order to find out whether it is the α- or the β-substituent that enforces the unusual conformation of **1**. In these calculations we started from our X-ray data and rotated the morpholino ligand by 90, 180, and 270° about the C(6)–N bond while we held the remaining structural parameters constant. The conformers resulting from those rotations are shown in Figure 4. In the experimentally found structure (**a**) the hydrogen atoms on C(23) and C(20) on the one hand and H(4) on the other are separated by more than 2 Å. Rotation of the morpholino ligand by 90° (**b**) results in a structure where the distances between hydrogen atoms on C(20) and H(4) and on C(23) and C(9) are smaller than 1.5 Å. Similarly, rotation by 180° leads to a structure (**c**) with distances smaller than 1.5 Å between hydrogens on C(20) and C(9) and on C(23) and C(10). Finally, rotation by 270° (**d**) yields qualitatively the same structure as rotation by 90°.

To obtain at least a rough estimate for the relative energies of these conformers we now calculated their heats of formation with the MNDO method optimizing only the positions of the hydrogen atoms. As expected, the lowest energy was obtained starting from the experimentally found structure, followed by the conformer obtained starting from **c**. The conformers obtained from **b** (90°) and **d** (270°) are quite similar in energy but significantly less stable than those resulting from **a** and **c**.

These results show that the experimentally found relative orientation of the morpholino ligand and the double bond in **1** is due to the presence of both, the α- and the β-substituent. The fact, however, that the nitrogen lone pair and the C=C bond are rather trans

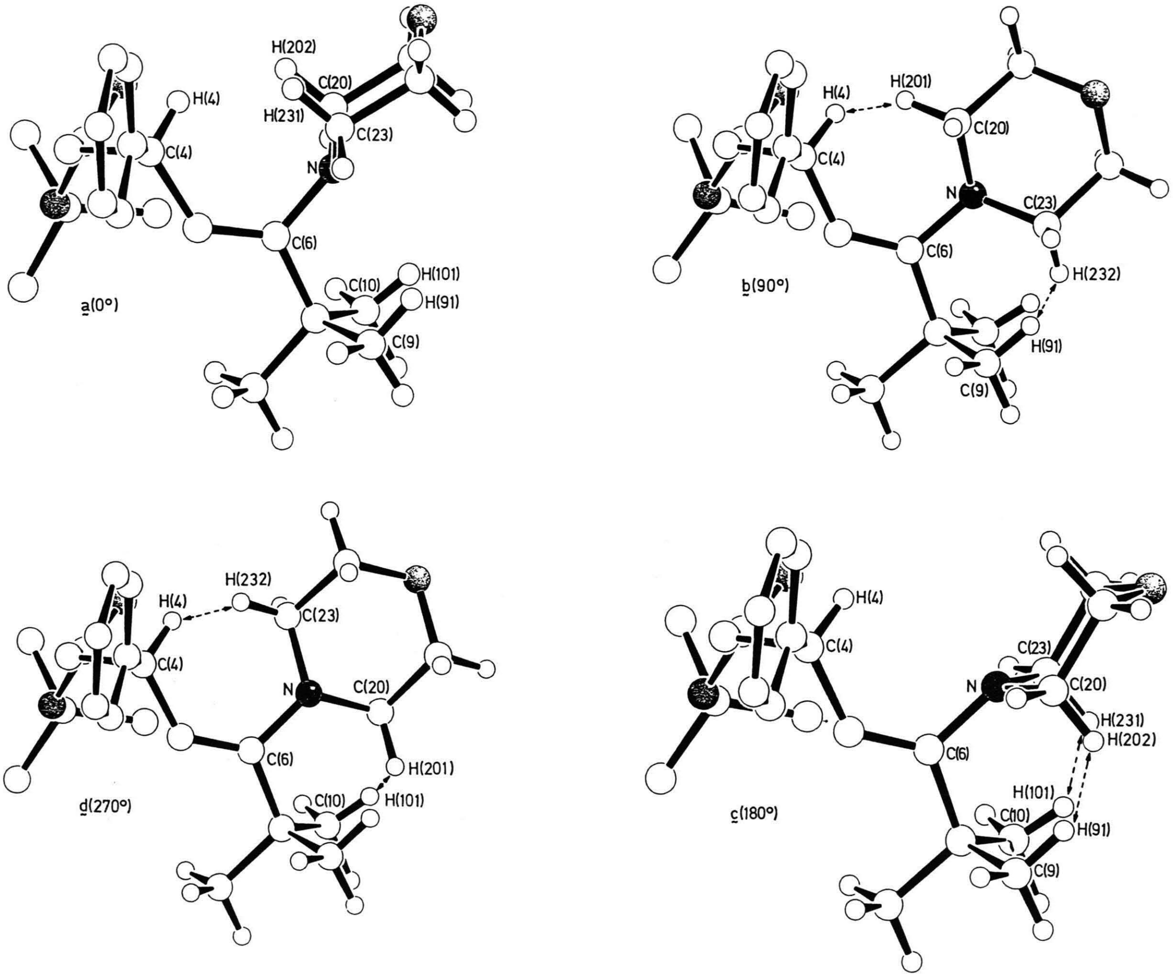
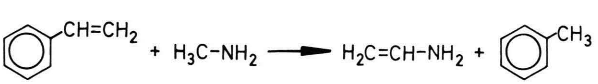


Fig. 4. Conformations **b**, **c**, and **d** have been obtained from the experimental solid state structure of **1** (**a**) by rotation about the N−C(6) axis. The rotation angles are 90°, 180°, and 270° in **b**, **c**, and **d**. The arrows indicate distances shorter than 1.5 Å.

than cis to each other is obviously due to the t-butyl group at the α-carbon atom.

While a simultaneous conjugation of the double bond with both the aromatic π-system and the nitrogen lone pair in **2** seems unlikely for steric reasons, the question remains why it is just the second interaction that prevails. To provide at least a tentative answer, we calculated the heat of reaction associated with the hypothetical process



Scheme 3

Using the heats of formation ΔH_f(styrene) = 35.12 kcal/mol [22], ΔH_f(methylamine) = −6.69 kcal/mol [22], ΔH_f(toluene) = 11.94 kcal/mol [22], and ΔH_f(vinylamine) = 10.41 kcal/mol [e], we obtained a heat of reaction of $\Delta H_r = -6.08$ kcal/mol. Assuming that this gain of energy is mainly due to conjugation of the nitrogen lone pair with the C=C double bond, we conclude that the latter interaction is indeed favoured over the Ph−CH=CH$_2$ resonance.

We further calculated the change of energy associated with the isodesmic reaction

$$\underset{\text{cis or trans}}{\text{4-vinylmorpholine}} + \underset{\text{planar}}{\text{styrene}} \longrightarrow \underset{\text{fully optimized}}{\text{4-vinylmorpholine}} + \underset{\text{orthogonal}}{\text{styrene}}$$

Scheme 4

Employing 6-31G//6-31G total energies (cf. Table 4 and E_{tot}(styrene, planar) = −307.478985 a.u., E_{tot}(styrene, orthogonal) = −307.474009 a.u.; both optimized under constraint of C_s symmetry) we obtained $\Delta E_r = -4.11$ kcal/mol using trans- and $\Delta E_r = -2.13$ kcal/mol employing cis 4-vinylmorpholine. Although these numbers confirm our thermochemical considerations, they are quite small and it is unlikely that this small energy difference is the only reason for the experimentally observed conformation. Indeed, rotating the phenyl group of **2** in a position where it is coplanar with the olefinic system shows that in such a conformation infavourable interactions between H(4) and one ortho proton of the aromatic ring will occur. Repulsive interaction between the aromatic hydrogen atoms with those at C(18) of the morpholino ligand will play a minor role. Finally we replaced the β-substituents in **1** and **2** by methyl groups and optimized the resulting structures with the AM1 method [9]. In both cases the characteristic features discussed above are retained during optimization. Moreover, calculation of the vibrational frequencies confirmed that the resulting structures are minima.

4. Conclusion

The unusual solid state structure of **1** is a result of the simultaneous presence of a bulky β-substituent and a spacious t-butyl group in α-position. In the case of 4-vinylmorpholine a structure where the nitrogen lone pair is almost parallel to the π system is lowest in energy, followed by the cis conformer. The presence of an α-t-butyl group and a bulky β-substituent Z to the morpholino ligand in that conformer, however, would lead to a significant repulsive interaction between the hydrogen atoms on C(20) and C(23) on the one hand and those of the methyl groups of the t-butyl substituent and C(4) on the other. While unfavourable interactions with two methyl groups of the t-butyl substituent will prevail in a cis species, this is not the case in what we call the trans isomer. As a result, the molecule takes the form which would be the least favourable one for the unsubstituted species.

In **2**, however, the β-substituent forces the relatively flat phenyl substituent into a position where no interference occurs. The nitrogen lone pair and the olefinic π system are more or less parallel in this case and conjugative interaction is possible.

Conjugation of the olefinic double bond with the aromatic π system would result in a structure with repulsive interactions between the ortho protons of the phenyl ring and H(4).

Optimization of closely related molecules in which the β-substituents have been replaced by methyl groups shows that the relative orientation of the α-substituents and the olefinic double bonds is maintained in the isolated species. Taking into account all these aspects, we conclude that, as far as the enamine parts are concerned, the gasphase structures of **1** and **2** might not differ significantly from those in the solid state.

5. Footnotes

[a] The term "ab initio" is also used by crystallographers to characterize direct methods. In this paper it is exclusively used in the sence of quantum chemistry, i.e., as a synonym for non-empirical quantum chemical methods.

[b] Employing the option PRECISE.

[c] For solution and refinement of the structure.

[d] While the calculations of Müller et al. [20] resulted in structures with a distinctly pyramidalized nitrogen atom, those of Sevin et al. [19] resulted in planar structures which contradict the experimental findings of Lovas et al. [21].

[e] The heat of formation of vinylamine has been calculated from the heat of reaction of the isodesmic process

$$H_2C{=}CH{-}NH_2 + CH_4 \longrightarrow H_2C{=}CH_2 + H_3C{-}NH_2$$

of $\Delta H_r = 13.3$ kcal/mol given in [23], employing ΔH_f(methane) $= -17.9$ kcal/mol [22] and ΔH_f(ethene) $= 12.5$ kcal/mol [22]. The result obtained in this way (ΔH_f(vinylamine) $=$ 10.41 kcal/mol) is not too different from the corresponding MINDO/3 (9.5 kcal/mol [24]) and AM1 (11.46 kcal/mol) values, while it is clearly smaller than the MNDO result (14.12 kcal/mol).

[f] Lists of structure factors, anisotropic displacement parameters, H atom coordinates, and tables of bond distances and angles may be obtained through the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, FRG, referring to CSD 55223, the authors, and the bibliographical data of [1].

[g] Ab initio geometries are available from the authors upon request.

[h] $U_{eq} = (1/3) \sum_i \sum_j U_{ij} \cdot a_i^* a_j^* \cdot \boldsymbol{a}_i \cdot \boldsymbol{a}_j$, where $\boldsymbol{a}_i$ is a

basis vector of the direct lattice, a_i^* the length of a basis vector of the reciprocal lattice, and U_{ij} an element of the displacement tensor.

Acknowledgement

The authors greatfully acknowledge the computer time provided by the Rechenzentrum der Rheinisch-Westfälischen Technischen Hochschule Aachen and the financial support by the Fonds der Chemischen Industrie.

We thank Prof. Dr. C. Krüger and Dr. S. Werner (Max-Planck-Institut für Kohlenforschung, Mülheim, FRG) for valuable discussions.

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