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The vibrational and NMR spectra, conformations and ab initio calculations of 1-aminoethylidene propanedinitrile and its N-methyl derivatives $\stackrel{\text{tr}}{\sim}$

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Abstract

The IR and Raman spectra of 1-aminoethylidene propanedinitrile (AE) $[H_2N-C(CH_3)=C(CN)_2]$, 1-(methylamino)ethylidene propanedinitrile (MAE) $[CH_3NH-C(CH_3)=C(CN)_2]$ and 1-(dimethylamino)ethylidene propanedinitrile (DMAE) $[(CH_3)_2N-C(CH_3)=C(CN)_2]$ were recorded as solids and solutes in various solvents in the region 4000–50 cm⁻¹. AE and DMAE can exist only as single conformers. From the vibrational and NMR spectra of MAE in solutions, the existence of two conformers with the methyl group oriented *anti* and *syn* towards the double C=C bond were confirmed. The enthalpy difference ΔH^0 between the conformers was measured to be 1.9 ± 1.3 kJ mol⁻¹ from the NMR spectra in DMSO solution.

Semi-empirical (AM1, PM3, MNDO, MINDO3) and ab initio SCF calculations using a DZP basis set were carried out for all the three compounds. The calculations support the existence of two conformers *anti* and *syn* for MAE with *anti* being 9.4 kJ mol⁻¹ more stable than *syn* from ab initio and 7.4, 12.0, 7.8 and 9.2 kJ mol⁻¹ from AM1, PM3, MNDO and MINDO3 calculations, respectively.

Finally, complete assignments of the vibrational spectra for all the three compounds were made with the aid of normal coordinate calculations employing scaled ab initio force constants. The scale factors from the similar aminomethylene propanedinitrile and its *N*-methyl derivatives were used and a very good agreement between calculated and experimental frequencies was achieved. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Vibrational and NMR spectra; Conformational analysis; Enamines; Semi-empirical and ab initio calculations

1. Introduction

Enamines are highly reactive compounds which are very important in a number of synthetic processes [1,2]. An aminoethylene derivatives of the general formula $R_1R_2N-CR_3=CXY$, where R_1 , R_2 and R_3 are H, alkyl or (hetero)aryl and X and Y are electron withdrawing groups, which are useful as materials for pharmaceutical, dye and polymer synthesis. Aminomethylene- ($R_3 = H$) and 1-aminoethylidene- ($R_3 = CH_3$) propanedinitrile and their homologues with the general formula $R_1R_2N-CR_3=C(CN)_2$ represent a group of compounds which also have a wide use in organic synthesis [3] and they are often used as

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Fig. 1. IR spectrum of AE in KBr pellet at room temperature.

starting reactants or intermediates for the preparation of many compounds.

2. Experimental

2.1. Preparative

The compounds were prepared according to the following reaction scheme:

$$R_1R_2NH + RO-C(CH_3) = C(CN)_2$$

 $\rightarrow R_1R_2N-C(CH_3) = C(CN)_2 + ROH$

Details of the synthesis have been described in a previous article [4]. The purity and melting points were determined by differential scanning calorimetry using a Perkin–Elmer DSC-7 calorimeter. The purity of all three compounds was better than 98% and the melting points are 225°C for AE, 150°C for MAE and 59°C for DMAE. Identity and purity of the samples were also confirmed by mass and by NMR spectroscopy.

2.2. Spectra

Mid-IR spectra in the region $4000-200 \text{ cm}^{-1}$ were

Despite the wide use in organic synthesis, their physico-chemical properties have not been studied in detail until now. Aminomethylene propanedinitrile and its *N*-methyl derivatives ($R_3 = H$ and R_1 and R_2 are H or CH₃) have been subjected to our former spectroscopic (IR, Raman, NMR) and ab initio conformational study [4]. This work represents an extension of these studies on 1-aminoethylidene propanedinitrile and its *N*-methyl derivatives ($R_3 =$ CH₃ and R₁ and R₂ are H or CH₃).

According to our knowledge 1-aminoethylidene propanedinitrile (AE) $[H_2N-C(CH_3)=C(CN)_2]$, 1-(methylamino)ethylidene propanedinitrile (MAE) $[CH_3NH-C(CH_3)=C(CN)_2]$ and 1-(dimethylamino)ethylidene propanedinitrile (DMAE) $[(CH_3)_2N-C(CH_3)=C(CN)_2]$ have not been yet investigated by vibrational or NMR spectroscopy.

To extend the information about the structure of these molecules we have also carried out an ab initio study with fully optimized geometries, a determination of the force fields and a calculation of frequencies for the normal modes of vibrations.



Fig. 2. Raman spectrum of solid AE at room temperature.

Table 1

Infrared and Raman spectral data (weak bands in the regions 4000-3500 and 2800-2300 cm⁻¹ have been omitted) for 1-aminoethylidene propanedinitrile (AE)

Infrared			Raman		Interpretation
Liquid (CH ₃ CN) ^a	Solid		Liquid (CH ₃ CN) ^a	Solid	
	KBr pellet	Nujol			
3420 ^b m	3465 w	3466 w			
3357 s	3353 s	3352 s		3356 w	ν_1
3253 s	3206 s	3205 s	3253 vw	3205 m	ν_2
3201 m,sh	3096 w,sh	3096 w,sh			
				3028 vw	ν_3
	2924 vw			2933 m	ν_4, ν_{23}
	2834 w			2834 vw	
2216 vs	2221 vs	2222 vs	2216 vs	2219 vvs	ν_5
2196 s,sh	2199 vs	2199 vs	2196 s,sh	2200 vvs	ν_6
2157 vw	2159 m,sh	2159 m,sh		2159 w	
	2125 w,sh	2125 w,sh			
	1833 vw	1832 vw			
1658 vs	1673 vs	1672 vs	1653 w	1671 m	ν_7
	1623 vvw	1629 vvw		1629 vvw	
	1572 w,sh	1573 w,sh		1570 vw	
1558 vs	1550 vs	1548 vs	1554 w	1542 w	ν_8
	1500 vw			1508 vw	
	1468 vw			1460 w,sh	ν_{24}
				1439 m	ν_{9}, ν_{10}

Table 1 (continued)

Infrared			Raman	Interpretation		
Liquid (CH ₃ CN) ^a	Solid		Liquid (CH ₃ CN) ^a	Solid		
	KBr pellet	Nujol				
	1374 m			1373 w	$ u_{11}$	
	1340 w,sh	1341 w,sh				
	1310 vw,sh	1309 vw, sh				
1238 w	1248 w	1248 w	1240 m	1250 s	ν_{12}	
	1218 vw	1217 vw		1220 vvw		
1158 w	1168 mw	1168 mw	1160 vw	1169 w	ν_{13}	
	1149 w	1149 w		1150 vw		
	1085 vw	1085 vw		1085 vvw		
	1053 vw	1054 vw			ν_{25}	
	1025 w	1026 w		1029 w	ν_{14}	
	988 vw				14	
962 w	964 w	987 vw		963 w	v_{15}	
	946 w	963 w		946 vw	- 15	
	895?	893 vvw				
	802 vw.sh	803 vw sh				
625 s	714 s. brd	709 s.sh			ν_{26}	
658 m sh	671 m	671 m	658 s	670 vs	V 16	
	662 m sh	665 m sh	0000	010 10	- 10	
	002 mjon	000 111,511		616 w		
606 w	609 m	609 m	605 w	609 w	V17	
000 11	548 mw	548 mw		548 w	V 17	
536 vw	543 w sh	542 w sh	533 w	544 w	V 19	
511 m	516 s	517 s	555 W	516 vw	V 18	
467 w	473 w	473 w		476 vw	P 28	
440 m	448 s	448 s	438 w	449 m	V 29	
110 111	390 w	389 w	100 11	394 m	P 19	
	570 W	507 11		348 yyw brd	► 20	
		$\sim 250?$		~ 2502	Vac	
		250.		193 s	P 30	
				175 vs	V 31	
				175 VS	V 21	
				124 vs	V <u>22</u>	
				112 w ch	V 32	
				03 w	11	
				25 w 86 c	V 33	
				65.		
				0.3.8		

^a Solvent used.

^b Abbreviations used are s: strong; m: medium; w: weak; v: very, sh: shoulder; brd: broad.

recorded on Bruker model IFS 88 and on Philips model PU9800 FT-IR spectrometers. The mid-IR spectra at room temperature of all the three compounds were measured as KBr pellets and as Nujol suspensions. Because the samples are not soluble in CCl₄ or CS₂, we used CH₃CN, CH₂Cl₂ and CHCl₃ as solvents. The solubility increased in the order AE, MAE, DMAE. The IR spectra of the solutions were measured in a cell equipped with KBr windows and a variable path length.

Raman recordings using an argon ion laser was impossible for each of the three samples due to extremely high fluorescence. Therefore, a Bruker RFS 100 instrument equipped with Nd³⁺:YAG laser was used. Raman spectra at room temperature of powdered solids were obtained for all three samples in the region



Fig. 3. IR spectrum of MAE in KBr pellet at room temperature.



Fig. 4. Raman spectrum of solid MAE at room temperature.



Fig. 5. IR spectra (top) of MAE as a solution in acetonitrile (curve a) and in KBr pellet (curve b); Raman spectra (bottom) of MAE as a solute in acetonitrile (curve a) and as a powdered solid (curve b) at room temperature. Dashed lines are the corresponding spectra of pure solvent.

 $4000-50 \text{ cm}^{-1}$. Owing to the low solubility, more than a 1000 scans were recorded to obtain the Raman spectra in acetonitrile solution.

The ¹H and ¹³C NMR spectra were run at room temperature on a Bruker MSL 300 spectrometer. To obtain a frequency resolution of 0.23 Hz/point, zero filling up to 64k was used for gated decoupled spectra before transformation.

3. Results

A mid-IR survey spectrum of AE as a KBr pellet is shown in Fig. 1 while a Raman spectrum as a solid powder is given in Fig. 2. The wave numbers of the observed IR and Raman bands are listed in Table 1.

The corresponding spectra of MAE are shown in Figs. 3 and 4, respectively. The IR and Raman spectra of the solid are compared in Fig. 5 with those of the acetonitrile solution in the region 750-450 cm⁻¹. Some weak Raman bands in acetonitrile solution vanishing in the solid spectra are demonstrated in

Fig. 6. The experimental wave numbers for MAE are collected in Table 2.

A mid-IR spectrum of DMAE as a KBr pellet appears in Fig. 7 whereas a Raman spectrum of a solid powder is given in Fig. 8. The wave numbers of the observed IR and Raman bands are listed in Table 3.

A comparison of the ¹³C NMR spectra of all the three samples in DMSO solution appears in Fig. 9, while the chemical shifts and vicinal coupling constants are listed in Table 4.

3.1. Conformational analysis

Similarly as for aminomethylene propanedinitrile and its *N*-methyl derivatives studied earlier [4] the conformational possibility for all the three samples is determined by the rotation around the C–N bond. We can again suppose that the stable configuration of the amino group is the one where the lone electron pair at the amino nitrogen atom is included in a highly conjugated system of the C=C double bond and the triple bonds of both cyano groups. Then it is obvious that AE and DMAE can exist only as a single conformer independent of the structure of the amino group (pyramidal or planar). It means that only MAE can exist in two conformations with the methyl group oriented out from the C=C double bond—*anti* conformer and towards the C=C double bond—*syn* conformer:



In the case of (methylamino)methylene propanedinitrile [(NC)₂C=CH–NHCH₃] studied earlier, the *anti* conformer was found to be more stable by 3.7 ± 1.4 kJ mol⁻¹ from the IR spectra in acetonitrile solution and by 3.4 ± 1.1 kJ mol⁻¹ from the NMR spectra in DMSO solution [4]. For MAE, we can also intuitively assume from steric reasons that again the *anti* conformer will be the more stable one, but due to the repulsion of the olefinic methyl group, a lower energy difference between conformers can be expected.

All the three samples have a very small vapour pressure and low solubility in most solvents. AE is soluble only in small amounts in more polar solvents

 (CH_3CN) and only the strongest bands could be observed in the IR solution spectra. The best soluble compound is DMAE and for this sample also the IR spectra in less polar solvent $(CH_2Cl_2 \text{ and } CHCl_3)$ could be obtained. No bands were missing in the solution spectra of these two compounds compared to the solid phase spectra.



Fig. 6. Raman spectra of MAE in acetonitrile solution (curve a) and as a powdered solid (curve b) at room temperature. Dashed lines are the Raman spectra of acetonitrile.



Fig. 7. IR spectrum of DMAE in KBr pellet at room temperature.



Fig. 8. Raman spectrum of a solid DMAE at room temperature.

Table 2

Infrared and Raman spectral data (weak bands in the regions 4000–3400 and 2800–2300 cm⁻¹ have been omitted) for 1-(methylamino)ethylidene propanedinitrile (MAE)

Infrared			Raman		Interpretation	
Liquid (CH ₃ CN) ^a	Solid		Liquid (CH ₃ CN) ^a	Solid	anti	syn
	KBr pellet	Nujol				
3332 s ^b	3361 m,sh	3360 w,sh	3325 vw			
	3281 s	3278 s		3283 vw	ν_1	
	3210 m,sh					
	3173 m,sh	3170 m,sh				
	3040 vw			3038 vw	ν_2	
	3011 vw			3012 w	ν_3	
	2978 vw			2975 w	ν_{28}, ν_{29}	
	2948 w			2948 m	ν_4	
				2937 m	ν_5	
	2886 vw,sh			2883 w		
	2849 vw,sh			2846 vw		
	2827 w					
2210 vs	2216 vs	2215 vs	2210 vvs	2216 vvs	ν_6	
2200 vs	2194 vs	2193 vs	2201 vs,sh	2195 vs	ν_7	
2172 w,sh	2169 m,sh	2168 s,sh	2173 m,sh	2171 m		
	2157 w,sh	2156 w,sh		2157 w		
	2141 vw,sh	2142 w,sh		2143 vw		
	1939 vw	1938 vw				
	1860 vw	1859 vw				
1602 vs	1611 vs	1608 vs	1601 m		ν_8	
	1590 vs	1584 vs		1590 m		
			1577 w,sh	*		ν_8
	1535 w,sh	1536 w,sh		1538?		-
1480 vw			1480 s	1472 s	$\nu_9, \nu_{10}, \nu_{11}$	
1460 w	1452 m				ν_{30}, ν_{31}	
1417 w,sh	1412 w,sh	1411 vw,sh	1416 s	1411 m	ν_{12}	
1409 s	1399 m	1398 w		1401 w,sh	ν_{13}	
1370?	1362 m	1365 m		1367 w	ν_{14}	
1350 vvw,sh	*		1350 w	*		ν_{14}
1328 vw	1326 w,sh			1327 vvw		
1246 m	1247 m	1246 m	1246 s	1247 s	ν_{15}	
	1234 w,sh			1235 w,sh		
			1228 w,sh	*		ν_{15}
			1215 vw	1217 vw		
1194 vw	1199 vw	1199 vw				
1175 vw	1166 w	1166 w	1173 vw	1167 vw	ν_{16}	
1127 vvw	1132 vw	1133 vw	1120 vvw	1133 vvw	ν_{32}	
1097 vw	1097 w,sh	1098 w,sh				
	1083 w,sh	1082 w,sh		1083 vw	ν_{17}	
1071 w	1069 m,sh	1068 m,sh	1070 vw	1070 w	ν_{33}	
	1063 m	1062 m			ν_{18}	
	1028 w	1028 w	1033 vvw	1028 vw		
	986 vw	986 vw				
	951 vw	951 vvw				
949 vw	924 w	924 w		925 w	ν_{19}	
	823 w,sh	820 w,sh				
	800 w	800 w				
754 w,sh				751 vw		

Table 2 (continued)

Infrared			Raman		Interpretation	
Liquid (CH ₃ CN) ^a	Solid		Liquid (CH ₃ CN) ^a	Solid	anti	syn
	KBr pellet	Nujol				
707 m	730 s,brd	729?	711 vvw?	724 vw	ν_{34}	
	695 m,sh	693 m,sh	690 s	696 s	ν_{20}	
679 m	*					ν_{34}
			636 mw	*		ν_{20}
621 w	*					ν_{21}
				613 w,sh		
610 vw	610 m	610 m	611 m	609 m	ν_{21}	
586 vw	*		585 vw,sh	*		ν_{22}
	566 vw	564 vw				
522 w	527 m	527 m	521 w	528 w	ν_{35}	
	521 vvw	521 vvw		521 w	ν_{22}	
510 m	510 s	510 s	504 vw,sh	514 w	ν_{36}	
				476 m,sh		
464 mw	471 m	471 m	465 s	470 s	ν_{37}	
	467 m,sh	464 w,sh				
	442 w,sh	444 w		449 w	ν_{23}	
	423 vw,sh	420 vw		420 vw		
	401 vw	402 vw		400 w	ν_{24}	
				383 vw		
		328 w	323 vw	331 w	ν_{25}	
			261 w	*		ν_{25}
		217?	211 w	222 w	ν_{38}	
				168 s,sh	ν_{39}	
			155 vs	154 vs	ν_{26}	
			143 s	142 s,sh	ν_{27}	
				111 s	ν_{40}	
				89 s	ν_{41}, ν_{42}	
				78 m,sh		
				56 m		

^a Solvent used.

^b Abbreviations used are s: strong; m: medium; w: weak; v: very; sh: shoulder; brd: broad; * denotes bands vanishing in the solid phase.

Relatively good IR spectra could be obtained for MAE in acetonitrile solution, but only weak spectra were measured for solution in less polar solvents (CH_2Cl_2) due to the very low solubility. Also several Raman spectra of MAE in acetonitrile solution were recorded. Unfortunately, even in the case of an almost saturated solution, the Raman bands are weak and rise only slightly above the noise level after averaging up to 4000 scans. Despite this, the Raman spectra of the solid sample and of the acetonitrile solution may be compared, as can be seen in Figs. 5 and 6. From the comparison of the IR and Raman spectra in solution and in the solid phase, we have found some bands

which disappear in the latter spectra. These bands are located in acetonitrile solution at 1577, 1350, 1228, 636, 621, 585 and 261 cm⁻¹. These facts support the conclusion that MAE exists in two conformational forms in acetonitrile solution.

These results were also confirmed by NMR spectroscopy. The ¹³C and ¹H NMR spectra of AE, MAE and DMAE in DMSO were measured at room temperature (Fig. 9). In these spectra each main band has a weaker counterpart only in the spectrum of MAE, meaning that the room temperature is below the coalescence temperature and confirming the existence of two conformers for this sample. Table 3 Infrared and Raman spectral data (weak bands in the regions 4000-3100 and 2800-2300 cm⁻¹ were omitted) for 1-(dimethylamino)ethylidene propanedinitrile (DMAE)

Infrared			Raman	Interpretation			
Liquid		Solid		Liquid (CH ₃ CN) ^a	Solid		
CH ₂ Cl ₂ ^a	CH ₃ CN ^a	KBr pellet	Nujol				
	3020 vw ^b	3018 vw		3021 mw	3018 m	ν_1	
	2989 w	2991 w		2985 m	2988 w,sh	ν_2, ν_3	
					2975 m	ν_4, ν_5	
	2951 w,sh	2960 w,sh			2958 w,sh	ν_6	
2941 m	2940?	2941 mw			2940 s	ν_{7}, ν_{8}	
		2922 w,sh			2923 w,sh	ν_9	
2890 w	2889 w	2887 vw		2886 vw,sh	2888 w	$\nu_{14} + \nu_{19} = 2894$	
2850 vvw	2848 vvw	2848 w				$2\nu_{19} = 2848$	
	2824 w	2823 vw			2825 vw	$\nu_{19} + \nu_{20} = 2833$	
2815 w		2811 vw,sh		2817 mw	2812 w	$2\nu_{20} = 2818$	
2254 w						20	
		2226 w,sh	2230 vw				
2209 vs	2206 vs	2202 vs	2203 vs	2205 vs	2201 vs	ν_{10}	
2191 vs	2188 vs	2181 vs	2178 vs	2186 vs	2182 vs	ν_{11}	
2149 w	2146 w	2142 w.sh	2143 w,sh	2144 w	2142 w	11	
		2136 w.sh	2136 w.sh		2136 vw		
1857 vw	1857 vw	1860 vw	1859 vvw				
		1640 w.sh	1637 w.sh	1643 vw	1646 vw		
1579 vs	1585 vs	1585 vs	1584 vs	1585 mw	1590 w	ν_{12}	
		1575 s.sh			1576 w	12	
		1551 s.sh	1553 s.sh			ν_{13}	
1471 m.sh	1470 m.sh	1468 m.sh		1468 m.sh	1467 m.sh	ν_{14}, ν_{15}	
1453 m	1457 m	1456 m		1454 m	1451 m	ν_{16}, ν_{17}	
		1430 m.sh			1428 w.sh	ν_{18}	
1424 s	1425 s	1423 s	1427?		1419 s.sh	ν_{10}	
1415 s	1414 s	1409 s	1407?	1415 s	1411 s	ν_{20}	
		1383 m			1383 m	ν_{21}	
1378 ms		1376 m.sh			1376 mw	ν_{22}	
		,			1270 w.sh	- 22	
	1264 m	1261 mw	1260 mw	1264 m	1263 mw	ν_{22}	
1218 vw.sh	1219 vw	1216 vw	1216 vw	1220 m	1216 m	ν_{23}	
1171 vw.sh	1212 1	1210	1169 vw.sh	1220 111	1170 w.sh	- 24	
1158 m	1161 m	1156 w	1155 w	1161 m	1158 m	V25. V26	
1099 vw		1098 vw	1099 vw			ν_{23} , ν_{20}	
10,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		10,0 11	1077 111		1086 vw	V 29	
1074 w	1076 w	1072 w	1072 w	1077 vw	1000 111	- 28	
1071 11	10/0 11	1064 vw sh	1063 vw sh	10// / //	1064 vw	Vao	
1050 m	1052 m sh	1046 w	1045 w	1050 vw	1046 vw	V 29	
1000 111	1002 111,011	1010	10.00 11	1000 11	1027 vw sh	- 30	
1019 s	1020 s	1018 s	1018 s	1022 w	1020 w	V21	
934 vw	941 vw	940 vw	939 vw	1022 11	940 vw	- 51	
839 w	840 w	837 vw	836 vw	840 vw	838 w	1/22	
007 11	010 ₩	821 yw sh	819 w sh	010 11	000 #	* 32	
802 w sh?	803 vw?	803 w	802 w				
002 w,511:	005 VW:	647?	647?	642 s	648 m	<i>V</i> ₂₂	
		621 m ch	621 m sh	072 3	621 s	V 33	
617 s	617 s	617 s	617 s	618 s	618 s ch	V 34	
01/ 5	017.5	017.5	017.5	010.5	010 5,511	× 35	

Table 3 (continued)

Interpretation
(CH ₃ CN) ^a Solid
569 vvw?
545 vw ν_{36}
532 w ν_{37}
490 vvw
w 470 m ν_{38}
452 m ν_{39}
s 430 m ν_{40}, ν_{41}
306 m ν_{42}
278 w ν_{43}
? ν_{44}, ν_{45}
175 vs $\nu_{46}, \nu_{47}, \nu_{48}$
? ν_{49}
85 vs,sh ν_{50}
73 vs ν_{51}

^a Solvents used.

^b Abbreviations used are s: strong; m: medium; w: weak; v: very; sh: shoulder.



Fig. 9. $^{13}\!C$ NMR spectra of AE, MAE and DMAE in DMSO solution at room temperature.

Compound	$AE R_1 = R_2 = H$	MAE: anti $R_1 = CH_3$, $R_2 = H$	MAE: syn $R_1 = H$, $R_2 = CH_3$	DMAE $R_1 = R_2 = CH_3$
¹³ C chemical shi	fts ^a in ppm			
C ₁	48.0	47.0	45.9	47.6
C ₂	172.6	172.2	168.2	168.9
C ₁₀	117.0	117.4	118.0	118.7
C ₁₂	115.3	115.6	117.0	117.5
C ₅	19.8	16.8	21.7	20.4
C ₄		31.0		42.8
C ₆			31.3	42.8
¹ H chemical shif	îts ^a in ppm			
H_4	8.66		8.86	
H _{14,15,16}		2.90		3.24
H ₆	8.37	8.60		
H _{17,18,19}			3.08	3.24
Vicinal coupling	constants ^a in Hz			
H_4-C_1 (trans)	9.2		7.9	
H_6-C_1 (cis)	4.6	3.7		
H_4-C_5 (cis)	4.2		2.8	
H_6-C_5 (trans)	7.5	5.6		

Table 4 ^{13}C and ^1H NMR data of the compounds $R_1R_2N\text{-}C(\text{CH}_3)\text{=}(\text{CN})_2$

^a Numbering of the atoms according to Figs. 10 and 11.



Fig. 10. Internal coordinates for AE ($X_4=X_6=H$), anti MAE ($X_4=C$, $X_6=H$) and syn MAE ($X_4=H$, $X_6=C$).

Compound	Method	$t(C_1 = C_2 - N_3 - X_4)^a$	$t(C_1 = C_2 - N_3 - X_6)$	$t(C_5 - C_2 - N_3 - X_4)$	
AE	Ab initio	180.14	-0.05	0.15	
	AM1	179.98	-0.01	0.00	
	PM3	156.40	23.12	-28.02	
	MNDO	153.87	23.36	-31.14	
	MINDO3	179.99	0.01	-0.02	
anti MAE	Ab initio	177.33	1.25	-3.01	
	AM1	180.00	0.00	0.00	
	PM3	158.87	20.89	-25.50	
	MNDO	157.50	5.16	-25.29	
	MINDO3	179.99	-0.02	-0.03	
syn MAE	Ab initio	179.96	0.13	0.14	
	AM1	180.02	0.22	0.00	
	PM3	165.37	28.96	-26.87	
	MNDO	178.87	-23.60	-2.03	
	MINDO3	179.61	-0.44	-0.07	
DMAE	Ab initio	163.22	-21.44	-16.52	
	AM1	169.52	-15.83	-8.73	
	PM3	160.63	-64.28	-15.06	
	MNDO	106.64	-106.43	-73.35	
	MINDO3	97.21	-97.21	-82.79	

Torsional angles (in degrees) of the amino group for the AE, MAE and DMAE calculated by ab initio and semi-empirical methods

^a Numbering of the atoms according to Figs. 10 and 11.

3.2. Conformational energy difference

The enthalpy difference between the two conformers of the MAE in solution can be determined from the temperature studies of the appropriate part of the IR or Raman spectra. The best band pairs should be conformationally pure belonging to the *anti* and *syn* conformers with sufficient intensity and separation. Unfortunately, from all the MAE bands in acetonitrile solution mentioned earlier, we did not find such a band pair.

In contrast, well separated bands are found in the ¹H NMR spectra corresponding to the methyl group protons for both conformers. Therefore, we measured the ¹H NMR spectra in the temperature range 298–338 K. The band areas were used for determining the equilibrium constant *K* at different temperatures. By applying the van't Hoff equation we have determined ΔH^0 by plotting ln *K* versus 1/*T*, where $\Delta H^0/R$ is the slope of the line obtained by a least squares procedure. It is assumed that ΔH^0 does not depend on the temperature in such a short interval. A value $\Delta H^0(syn-anti) = 1.9 \pm 1.3 \text{ kJ mol}^{-1}$ was obtained, but due to short interval, uncertainty is relatively high.

3.3. Semi-empirical and ab initio calculations

As for aminomethylene propanedinitrile and its *N*methyl derivatives [4] studied previously, we also carried out semi-empirical and ab initio calculations to support the interpretation of the obtained experimental data. The semi-empirical AM1, PM3, MNDO and MINDO3 methods were employed using the MOPAC program [5]. For the ab initio Hartree– Fock SCF calculations the TURBOMOL program [6] and the standard Huzinaga DZP basis set [7,8] were employed. To improve the accuracy of the ab initio energies, MP2 corrections were carried out, but geometries of the molecules were not reoptimized at MP2 level.

A decreasing character of the pyramidal structure of the amino group due to conjugation of the nitrogen lone electron pair from CH_3NH_2 to $CH_2=CHNH_2$ has been measured [9,10]. In substituted aniline a planar

Table 5

Table 6

Ab initio structural parameters (bond lengths in angstroms, bond and torsion angles in degrees) for AE, MAE and DMAE

Name ^a	Internal coordinate ^b	AE	MAE		DMAE	
			anti	syn		
R1	$r(C_1 = C_2)$	1.3672	1.3739	1.3714	1.3780	
R2	$r(C_2 - N_3)$	1.3344	1.3339	1.3351	1.3409	
R3	$r(N_3-H_4)$	0.9954		0.9960		
R3	$r(N_3-C_4)$		1.4476		1.4540	
R4	$r(N_3-H_6)$	0.9986	0.9993			
R4	$r(N_2-C_6)$			1.4521	1.4567	
R5	$r(C_2-C_5)$	1.5002	1.5004	1.5074	1.5087	
R6	$r(C_1 - C_{10})$	1 4299	1.3001	1 4345	1.4339	
R7	$r(C_{10} \equiv N_{11})$	1.1348	1.1352	1,1348	1,1351	
R8	$r(C_1 - C_{12})$	1 4319	1 4306	1 4343	1 4330	
R9	$r(C_1 \equiv N_{12})$	1 1352	1 1357	1 1345	1 1348	
R10	$r(C_1 - H_2)$	1.0828	1.0826	1.0818	1.0824	
R10	$r(C_{2}-H_{2})$	1.0826	1.0820	1.0010	1.0866	
R12	$r(C_5 - H_6)$	1.0896	1.0090	1.0896	1.0896	
R12 R13	$r(C_1 - H_1)$	1.0070	1.0852	1.0070	1.0826	
R13	$r(C_4 - H_{14})$		1.0052		1.0873	
R14 R15	$r(C_4 - H_{15})$		1.0870		1.0075	
R15 P16	r(C H)		1.0077	1.0850	1.0834	
R10 P17	$r(C_{6}-H_{17})$			1.0853	1.0834	
R17 D19	$r(C_{6}-H_{18})$			1.0803	1.0870	
8 S	$(C_6 - H_{19})$	121.05	121 17	126.45	124.26	
0	$\angle (C_1 - C_2 - N_3)$	121.95	121.17	120.45	124.50	
φ	$\angle (C_1 - C_2 - C_5)$	122.30	121.45	120.32	110.72	
φ	$\angle (C_2 - N_3 - H_4)$	120.08	126 /1	114.97	122.24	
ψ	$((C_2 - N_3 - C_4))$	121.40	120.41		122.24	
μ	$\angle (C_2 - N_3 - H_6)$	121.49	110.94	120.40	102 (0	
μ	$\angle (C_2 - N_3 - C_6)$	100.12	100.05	129.49	123.62	
β	$\angle (C_2 = C_1 - C_{10})$	122.13	122.25	120.34	120.79	
Ŷ	$\angle (C_2 = C_1 - C_{12})$	119.55	119.63	125.12	124.48	
λ	$\angle (C_1 - C_{10} = N_{11})$	1/9.6/	179.73	1/9.6/	179.48	
κ	$\angle (C_1 - C_{12} = N_{13})$	1/6.50	1/6.40	1/8.04	177.82	
au	$\angle (C_2 - C_5 - H_7)$	112.03	111.40	112.60	110.96	
v_1	$\angle (C_2 - C_5 - H_8)$	109.24	109.70	109.15	110.81	
v_2	$\angle (C_2 - C_5 - H_9)$	109.23	109.96	109.13	109.86	
π	$\angle (N_3 - C_4 - H_{14})$		107.75		111.74	
θ_1	$\angle (N_3 - C_4 - H_{15})$		111.77		108.43	
θ_2	$\angle (N_3 - C_4 - H_{16})$		112.20		111.77	
ξ	$\angle (N_3 - C_6 - H_{17})$			107.18	110.52	
ψ_1	$(N_3 - C_6 - H_{18})$			111.72	107.71	
ψ_2	$(N_3 - C_6 - H_{19})$			111.71	112.56	
<i>t</i> 1	$t(C_1 = C_2 - N_3 - H_4)$	180.14		179.96		
<i>t</i> 1	$t(C_1 = C_2 - N_3 - C_4)$		177.33		163.22	
<i>t</i> 2	$t(C_1 = C_2 - N_3 - H_6)$	-0.05	1.25			
<i>t</i> 2	$t(C_1 = C_2 - N_3 - C_6)$			0.13	-21.44	
t3	$t(C_5 - C_2 - N_3 - H_4)$	0.15		0.14		
t3	$t(C_5-C_2-N_3-C_4)$		-3.01		-16.52	
<i>t</i> 4	$t(N_3 - C_2 = C_1 - C_{10})$	180.02	179.41	180.03	172.20	
<i>t</i> 5	$t(N_3-C_2=C_1-C_{12})$	0.02	-0.34	0.02	-14.17	
<i>t</i> 6	$t(C_1 = C_2 - C_5 - H_7)$	0.06	-2.51	0.67	18.16	
<i>t</i> 7	$t(C_1 = C_2 - C_5 - H_8)$	120.90	117.93	121.57	139.24	
<i>t</i> 8	$t(C_1 = C_2 - C_5 - H_9)$	239.21	236.64	239.82	259.28	

Name ^a	Internal coordinate ^b	AE	MAE		DMAE	
			anti	syn		
t9	$t(C_2 - N_3 - C_4 - H_{14})$		174.12		-25.61	
<i>t</i> 10	$t(C_2 - N_3 - C_4 - H_{15})$		55.76		216.26	
<i>t</i> 11	$t(C_2 - N_3 - C_4 - H_{16})$		-66.95		96.93	
<i>t</i> 12	$t(C_2 - N_3 - C_6 - H_{17})$			180.03	-27.28	
<i>t</i> 13	$t(C_2 - N_3 - C_6 - H_{18})$			61.17	214.89	
<i>t</i> 14	$t(C_2 - N_3 - C_6 - H_{19})$			-61.12	94.80	
11 ^c	$lc(C_2C_{10}C_1N_{11})$	0.33	0.27	-0.33	-0.45	
12 ^c	$lc(C_2C_{12}C_1N_{13})$	3.50	3.60	-1.96	-1.15	
13 ^c	$lp(C_2C_{10}C_1N_{11})$	0.00	-0.04	0.00	0.26	
14 ^c	$lp(C_2C_{12}C_1N_{13})$	0.00	0.04	-0.01	1.85	

Table 6 (continued)

^a Internal coordinate symbol.
 ^b Numbering of the atoms according to Figs. 10 and 11.

^c Coordinate describing linear part of molecule in degrees.



Fig. 11. Internal coordinates for DMAE.

Table 7		
Comparison of the observed	and calculated vibration	onal frequencies for AE

No.	Fundamental ^a	Observed ^b	Ab initio	Scaled ^c	PED ^d
Α′					
ν_1	NH ₂ asym stretch	3357	3939	3420	97 NH ₂ as
ν_2	NH ₂ sym stretch	3253	3802	3301	97 NH ₂ ss
ν_3	CH ₃ asym stretch	3028	3338	3054	92 CH ₃ as
ν_4	CH ₃ sym stretch	2933	3196	2924	93 CH ₃ ss
ν_5	C≡N stretch	2216	2587	2214	84 C≡N s
ν_6	C≡N stretch	2196	2578	2207	84 C≡N s
ν_7	NH ₂ deformation	1653	1802	1643	78 NH ₂ δ, 19 C–N s
ν_8	C=C stretch	1554	1723	1581	63 C=C s, 13 NH ₂ δ
ν_9	=C-N stretch	1439	1579	1438	24 C-N s, 26 CH ₃ aδ, 29 CH ₃ aδ
ν_{10}	CH ₃ asym bend	1439	1570	1436	56 CH ₃ aδ, 12 C–N s
ν_{11}	CH ₃ sym bend	1373	1507	1373	71 CH ₃ sδ, 12 C–N s
ν_{12}	CC ₂ asym stretch	1240	1344	1227	48 CC ₂ as, 11 C–N s
ν_{13}	NH ₂ rock	1160	1266	1154	38 NH ₂ ro, 19 CC ₂ as, 10 CC ₂ ss
ν_{14}	CH ₃ sym rock	1025	1112	1013	69 CH ₃ ro, 11 NH ₂ , ro, 10 C-N s
ν_{15}	=C-CH ₃ stretch	962	1036	949	47 C-CH ₃ s, 24 NH ₂ ro, 10 CC ₂ ss
ν_{16}	CC2 sym stretch	658	700	639	26 CC ₂ ss, 15 C=C s, 15 C-CH ₃ s
ν_{17}	CC ₂ deformation	605	668	603	26 CC ₂ δ , 26 CC \equiv N s δ , 26 CC ₂ ss
ν_{18}	C−C≡N asym bend	533	591	533	26 CC \equiv N a δ , 30 CC ₂ ro, 10 C $=$ CN δ
ν_{19}	C=C-N bend	438	471	426	55 C=CN δ, 17 CC≡N aδ
ν_{20}	=C-CH ₃ rock	394	427	386	67 CH ₃ ro, 19 CC≡N aδ
ν_{21}	CC ₂ rock	175	181	163	48 CC₂ ro, 33 CC≡N aδ
ν_{22}	$C-C\equiv N$ sym bend	151	156	139	61 CC \equiv N s δ , 54 CC ₂ δ
Α″					
ν_{23}	CH3 asym stretch	2933	3267	2989	100 CH ₃ as
ν_{24}	CH ₃ asym bend	1460	1592	1447	92 CH ₃ aδ
ν_{25}	CH ₃ asym rock	1053	1157	1057	70 CH ₃ ro
ν_{26}	C-C≡N sym bend	625	752	689	23 CC≡N sδ, 27 CC ₂ wa, 38 CH ₃ wa
ν_{27}	NH ₂ torsion	548	613	560	40 NH ₂ τ , 27 CC=N s δ , 6 CC ₂ wa
ν_{28}	=C-CH ₃ wag	511	555	512	38 CH ₃ wa, 36 NH ₂ τ, 15 CC≡N sδ
ν_{29}	C-C≡N asym bend	467	532	471	84 CC≡N aδ, 6 C=C τ
ν_{30}	NH ₂ wag		286	248	135 NH ₂ wa
ν_{31}	CC ₂ wag	193	207	190	62 CC₂ wa, 32 CC≡N sδ
ν_{32}	C=C torsion	124	122	114	108 C=C τ
ν_{33}	CH ₃ torsion	93	87	82	144 CH ₃ $ au$

^a Approximate assignment taking into account also the comparison of the spectra of all three samples.

^b Observed frequencies are from liquid if available.

^c Calculated using scaling factors mentioned in the text.

^d Potential energy distribution for scaled frequencies.

structure was calculated [11] due to electron-withdrawing groups in the benzene ring. Similarly, a nearly planar structure of the amino group is expected in the present molecules due to the strongly electronwithdrawing cyano groups. This is important for interpreting the vibrational spectra of the present molecules. If the amino group is planar and if the plane of the amino group is oriented in the plane of the rest of the molecule, the molecule may have C_s symmetry. Otherwise, the molecule lacks a plane of symmetry and has C_1 symmetry. In all the semi-empirical and ab initio calculations the full set of structural parameters were optimized with no assumptions regarding symmetry. The results of the torsional angles for the C=C(CH₃)–NR₁R₂ moiety (R₁ and R₂ is H or C) are summarized in Table 5.

From these results it is obvious that ab initio, AM1 and MINDO3 methods give planar structures of the amino group for AE and for both conformers of MAE. Very small non-planarity $(2-3^{\circ})$ for the anti conformer of MAE in the ab initio method is probably due to the steric repulsion of the olefinic methyl group. In all these cases the orientation of the methyl group follows the plane of the symmetry of the heavy atoms (again with small exception for the anti conformer of MAE in ab intio method) and we can accept in these methods for molecules the C_s symmetry. PM3 and MNDO give only non-planar pyramidal structures of the amino group for these molecules. When the plane of the symmetry was fixed, the obtained energies were significantly higher and the vibrational analysis gave one negative vibrational mode meaning that the planar structure can be a saddle point for inversion processes.

Unlike (dimethylamino)methylene propanedinitrile [4] studied earlier, for DMAE the ab initio as well as all semi-empirical methods suggest only significantly non-planar structures of the molecule probably due to steric interactions of the olefinic and amino methyl groups; the differences are only in the geometry of the amino group, while the ab initio and AM1 methods suggest practically planar structure of the C–NC₂ moiety, but turned 15–20° from the plane of the rest of molecule, the PM3, MNDO and MINDO3 methods give significantly pyramidal structure of the amino group orientated toward the olefinic methyl group. The last two methods give even the amino group turned symmetricaly perpendicular to the plane of rest of molecule.

As the most acceptable results, we consider the ab initio calculations which were calculated with a relatively large basis set. Refinement of the ab initio geometry was carried out until the norm of gradient was lower than 10^{-4} a.u. (most of them in the range 10^{-5}) and the vibrational analysis gave only nonnegative vibrational modes to ensure that it is an equilibrium structure and no saddle point. The obtained internal coordinates with their names and labelling according to Figs. 10 and 11 are listed in the Table 6. Since experimental structural data are not available for any of these molecules, the reliability of the ab initio structures is difficult to ascertain. Nevertheless, for interpreting the vibrational spectra, we have accepted planar structures with C_s symmetry for AE and MAE and a non-planar structure with C_1 symmetry for DMAE. The same conclusion regarding to the planarity of the amino group has been done in a recent theoretical study of the formamide, *N*-methylformamide, *N*,*N*-dimethylformamide, acetamide and *N*-methylacetamide [12]. The molecular structure of the mentioned compounds were investigated by ab initio Hartree–Fock, MP2 and density functional theory BLYP and B3LYP methods in conjunction with basis sets ranging from 6-31G^{*} to 6-311+G(2d,p) and at all levels of theory the heavy atom skeleton was found to be planar.

All the five mentioned computational methods suggest the *anti* conformer of MAE as more stable. From the ab initio calculations in a DZP basis set at HF/DZP SCF level the *anti* conformer is more stable by 12.3 kJ mol^{-1} . After including the MP2 corrections (calculated for SCF geometry) and zero point vibrational energy (ZPE), the *anti* conformer is at the MP2/HF/DZP level by 9.6 kJ mol⁻¹ and at the ZPE/MP2/HF/DZP level by 9.4 kJ mol⁻¹ more stable. For AM1, PM3, MNDO and MINDO3, the values 7.4, 12.0, 7.8 and 9.2 kJ mol⁻¹ were calculated.

3.4. Normal coordinate analysis

The calculated ab initio HF vibrational frequencies in a DZP basis set for all the three samples are given in Tables 7-10. In order to obtain a more complete description of the molecular motions involved in the normal vibration, we have carried out a normal coordinate analysis. It is well known that raw ab initio HF frequencies in different basis sets are systematically 10-15% higher that the observed fundamental vibrational frequencies [13], but after a suitable correction by one or several few scale factors they give an accurate prediction of the vibrational fundamentals [14]. Therefore, the ab initio force fields for all the three samples in the Cartesian coordinates calculated in a DZP basis set at the HF level were transformed to suitable internal coordinates and then subsequently scaled according to the type of internal coordinates, using the scheme [15]: F_{ii} (scaled) = F_{ii} (ab initio) $(x_i x_i)^{1/2}$, where x_i and x_i are the scaling factors for the diagonal constants. The eight scaling factors: 0.851 for

Table 8	
Comparison of the observed and calculat	ted vibration frequencies for anti MAE

No.	Fundamental ^a	Observed ^b	Ab initio	Scaled ^c	PED^{d}
Α′					
ν_1	N-H stretch	3283	3826	3322	99 NH s
ν_2	CH ₃ asym stretch	3040	3340	3055	93 (N)CH ₃ as
$\tilde{\nu}_3$	CH ₃ asym stretch	3011	3307	3025	93 (C)CH ₃ as
ν_A	CH ₃ sym stretch	2948	3204	2931	90 (N)CH ₃ ss
$\bar{\nu}_{5}$	CH ₃ sym stretch	2937	3191	2919	89 (C)CH ₂ ss
ν_6	C≡N stretch	2210	2582	2210	82 C≡N s
ν_7	C≡N stretci	2200	2571	2202	82 C≡N s
ν_8	N–H rock	1602	1773	1622	42 NH ro, 31 C=C s, 22 C-N s
ν_{9}	C=C stretch	1480	1636	1497	23 C=C s, 15 C–N s, 17 (N)CH ₃ aδ
ν_{10}	=C-N stretch	1480	1617	1473	12 C–N s. 50 (N)CH ₃ sδ. 14 (N)CH ₃ aδ.
ν_{11}	CH ₃ asym bend	1480	1612	1467	52 (N)CH ₃ aδ, 16 (C)CH ₃ aδ, 13 NH ro
ν_{12}	CH ₃ asym bend	1417	1569	1429	61 (C)CH ₂ aδ. 11 C=C s
ν_{13}	CH ₃ sym bend	1409	1549	1412	30 (N)CH ₃ sδ. 35 (C)CH ₃ sδ. 11 NH ro
ν_{14}	CH ₃ sym bend	1362	1505	1371	54 (C)CH ₂ sδ. 13 C–N s. 11 (N)CH ₂ sδ
ν_{15}	CC_2 asym stretch	1246	1360	1243	41 CC ₂ as. 17 N–CH ₃ s
ν_{16}	CH ₃ svm rock	1175	1289	1175	44 (N)CH ₃ ro. 18 CC ₂ as
ν_{17}	N–CH ₃ stretch	1083	1177	1078	34 N-CH ₃ s, 18 (C)CH ₃ ro, 13 (N)CH ₃ ro
ν_{19}	CH ₃ svm rock	1063	1156	1050	26 (C)CH ₂ ro
ν_{10}	C-CH ₂ stretch	949	1007	923	17 C-CH ₃ s. 22 N-CH ₃ s. 16 C-N s
ν_{20}	CC_2 sym stretch	690	736	673	15 CC ₂ ss. 26 C–CH ₃ s. 15 CNC δ
ν_{20}	CC_2 deformation	610	671	605	27 CC ₂ δ , 27 CC \equiv N s δ , 24 CC ₂ ss
ν_{22}	$C-C \equiv N$ asym bend	521	583	523	34 CC=N a δ , 32 CC ₂ ro
ν_{22}	C=C-N bend	449	500	456	11 C=CN δ , 28 CNC δ , 16 C-CH ₂ ro
ν_{24}	C−CH ₂ rock	400	429	387	46 C–CH ₃ ro. 23 C=CN δ. 24 CC≡N aδ
ν_{25}	C-N-C bend	323	326	296	38 CNC δ , 18 C=CN δ , 13 C-CH ₃ ro
ν_{25}	C–C≡N sym bend	155	165	147	33 CC=N s δ . 31 CC ₂ δ
ν_{27}	CC ₂ rock	143	145	131	26 CC₂ ro. 17 CC≡N aδ
A″					
V 200	CH ₂ asym stretch	2975	3276	2996	94 (N)CH ₂ as
ν_{20}	CH_2 asym stretch	2975	3266	2987	90 (C)CH ₂ as
ν_{29}	CH ₃ asym bend	1460	1605	1459	$60 (N)CH_3 a\delta$, 28 (C)CH ₃ a δ
v_{21}	CH_2 asym bend	1460	1589	1445	$60 (C)CH_2 a\delta$, 31 (N)CH ₂ a δ
ν_{22}	CH ₂ asym rock	1127	1240	1128	88 (N)CH ₂ ro
ν_{32}	CH ₃ asym rock	1071	1151	1054	46 (C)CH ₃ ro
ν_{24}	$C-C\equiv N$ sym bend	707	749	684	$23 \text{ CC} \equiv \text{N} \text{ s}\delta$, 25 CC_2 wa, $41 \text{ C} - \text{CH}_2$ wa
V25	N-H wag	522	619	556	24 NH wa. 10 C–N τ . 35 CC \equiv N s δ
v_{24}	C-CH ₂ wag	510	551	501	31 C-CH ₂ wa. 16 NH wa. 26 C-N τ
ν_{27}	$C-C\equiv N$ asym bend	464	537	474	85 CC=N a δ . 5 C=C τ
V28	CC ₂ wag	211	219	201	53 CC_2 wa. 26 CC \equiv N s δ
ν_{20}	$C-CH_2$ torsion	168	200	186	$37 \text{ C}-\text{CH}_3 \tau$, 20 N-CH ₃ τ , 10 C-N τ
ν_{40}	=C-N torsion	111	128	119	$14 \text{ C-N } \tau$, $74 \text{ C-CH}_2 \tau$, $41 \text{ C=C } \tau$
ν_{41}	C=C torsion	89	104	96	$61 \text{ C=C } \tau$
71 V 40	N-CH ₂ torsion	89	65	60	45° N–CH ₃ τ . 33 NH wa. 10 C–N τ

^a Approximate assignment taking into account also the comparison of the spectra of all three samples.
 ^b Observed frequencies are from liquid if available.
 ^c Calculated using scaling factors mentioned in the text.
 ^d Potential energy distribution for scaled frequencies.

^e Relative values.

No.	Fundamental ^a	Observed ^b	Ab initio	Scale ^c	PED^d
A′					
ν_1	N–H stretch		3866	3357	99 NH s
ν_2	CH ₃ asym stretch		3348	3063	90 (N)CH ₃ as
$\bar{\nu_3}$	CH_3 asym stretch		3305	3022	94 (C)CH ₃ as
ν_A	CH_3 sym stretch		3213	2939	$100 (C)CH_3 ss$
ν_5	CH ₃ sym stretch		3196	2924	91 (N)CH ₃ ss
ν_6	C≡N stretch		2587	2213	89 C≡N s
ν_7	C≡N stretch		2578	2208	87 C≡N s
ν_{\circ}	C=C stretch	1577	1746	1598	48 C=C s. 32 NH ro
ν_0	=C-N stretch		1710	1567	48 C–N s. 33 NH ro. 13 C=C s
ν_{10}	CH ₂ asym bend		1617	1471	89 (N)CH ₂ aδ
ν_{11}	CH_2 asym bend		1594	1450	43 (C)CH ₂ aδ. 32 (N)CH ₂ sδ
V10	CH_2 sym bend		1570	1430	$57 (N)CH_2 s\delta_2 29 (C)CH_2 a\delta_2$
V 12	CH_2 sym bend		1535	1398	$73 (C)CH_2 s\delta 13 (C)CH_2 s\delta 12 C-CH_2 s$
V 13	N-H rock	1350	1468	1342	73 (c)eng so, 15 (c)eng so, 12 c eng s 22 NH ro 19 C-N s 14 (C)CH ₂ s δ
V 14	CC, asym stretch	1228	1335	1217	32 CC_{2} as 20 (N) CH ₂ ro
V 15	CH ₂ sym rock	1220	1298	1185	$31 (N)CH_{2} ro 22 CC_{2} as 19 N-CH_{2} s$
V 16	N_CH ₂ stretch		1194	1091	26 N-CH ₂ s 28 (C)CH ₂ ro 11 CC ₂ as
V 17	$C - CH_{a}$ stretch		11/4	1045	$37 C - CH_{2} s \cdot 14 (C)CH_{2} ro \cdot 12 CC_{2} s s$
V 18	CH ₂ sym rock		1022	935	$33 (C)CH_{2}$ to $24 N_{2}$ CH ₂ s $13 C_{2}$ N s
V 19	CC. deformation	636	603	623	$33 \text{ CC}_{\circ} \text{ ss} 31 \text{ CC}_{=} \text{N} \text{ s} 321 \text{ CC}_{\circ} \text{ ss}$
V 20	CC_2 deformation	621	659	604	$35 CC_2 ss, 51 CCN sb, 21 CC_2 as$
<i>ν</i> ₂₁	C=C N band	586	634	577	$29 CC_2 0, 15 C-CH_3 s, 10 C-C s$
V ₂₂	C = C = N beind	580	514	450	$50 C = CN 0, 20 CNC 0 10 CC_2 10$ 53 CC = N 28 17 CC ro 20 CNC 8
V ₂₃	C = CH rock		126	439	$35 \text{ CC-N} ab, 17 \text{ CC}_2 10, 20 \text{ CNC} b$
<i>v</i> ₂₄	$C = C H_3$ lock	261	420	250	$50 C - CH_3 10$
V ₂₅	C-N-C bend	201	203	239	54 CNC 0, 29 C-CN 0
ν_{26}	CC_2 lock		190	1/1	$49 CC_2 10, 29 CC=N ab$
ν ₂₇	C-C=N sym bend		170	152	$01 \mathbf{CC} = \mathbf{N} \mathbf{so}, 50 \mathbf{CC}_2 \mathbf{o}$
A″			220.4	2022	
ν_{28}	CH_3 asym stretch		3304	3023	94 (C)CH ₃ as
ν_{29}	CH_3 asym stretch		3266	2987	$100 (N)CH_3$ as
ν_{30}	CH_3 asym bend		1598	1453	89 (N)CH ₃ ad
ν_{31}	CH_3 asym bend		1596	1451	82 (C)CH ₃ að
ν_{32}	CH ₃ asym rock		1238	1126	89 (N)CH ₃ ro
ν_{33}	CH ₃ asym rock		1157	1056	71 (C)CH ₃ ro
ν_{34}	$C-C \equiv N$ sym bend	679	743	679	28 CC \equiv N s δ , 32 CC ₂ wa, 42 C–CH ₃ wa
ν_{35}	C–CH ₃ wag		599	545	38 C−CH ₃ wa, 38 CC≡N sδ
ν_{36}	$C-C \equiv N$ asym bend		536	475	76 CC \equiv N a δ , 3 C $=$ C τ
ν_{37}	N–H wag		481	430	48 NH wa, 55 C–N τ
ν_{38}	N-CH ₃ torsion		210	194	91 N–CH ₃ τ , 23 C–N τ
ν_{39}	CC_2 wag		208	192	61 CC ₂ wa, 32 CC≡N sδ
ν_{40}	C=C torsion		176	161	16 C=C τ , 46 N–CH ₃ τ
ν_{41}	C-CH ₃ torsion		49	45	33^{e} C–CH ₃ τ , 26 C=C τ
ν_{42}	=C $-$ N torsion		37	34	33^{e} C–N τ , 31 C–CH ₃ τ

Table 9 Comparison of the observed and calculated vibrational frequencies for *syn* MAE

^a Approximate assignment taking into account also the comparison of the spectra of all three samples.

^b Observed frequencies are from liquid if available.

^c Calculated using scaling factors mentioned in the text.

^d Potential energy distribution for scaled frequencies.

^e Relative values.

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stretching, 0.827 for bending, 0.874 for torsion and out of plane, 0.754 for N-H stretching, 0.837 for C-H stretching, 0.720 for C≡N stretching, 0.750 for hydrogen wagging and 0.770 for C-C≡N linear bending coordinates obtained in the earlier vibrational study for similar molecules of aminomethylene propanedinitrile and its N-methyl derivatives [4] have been used. In the mentioned study, introducing the separate scaling factors for a well localized vibrational modes of the N-H, C-H and C≡N stretching coordinates, for the hydrogen wagging coordinates $(=C-H, -NH_2 \text{ and } -N-H \text{ wagging coordinates})$ and for the C–C \equiv N linear bending coordinates improved very much the agreement of the calculated and observed frequencies. These scale factors were optimized on the 85 experimental frequencies. Frequencies calculated with the mentioned scaling factors and the corresponding potential energy distributions (PED) for AE, anti and syn MAE and DMAE are given in Tables 7-10. Agreement with the experimental frequencies is up to 5% outside the low frequency region below 250 cm⁻¹ where data from the fluid phases are missing and the assignment is also rather uncertain due to the lattice modes.

4. Discussion

4.1. Geometry

As for aminomethylene propanedinitrile and its N-methyl derivatives [4], experimental structure data are also not available for the molecules studied. The reliability of the calculated geometrical values can be tested only in comparison with similar compounds. This was done previously, where a decreasing of the multiple character of the carbon-carbon double bond and increasing the carbon-nitrogen bond order due to interaction of the nitrogen lone electron pair with the π -electron system were confirmed [4].

The calculated C=C and C-N bond lengths for our enamines indicate a highly conjugated system and both are slightly longer than for the corresponding aminomethylene propanedinitrile and its *N*-methyl derivatives [4] studied earlier. It means that the substitution of an olefinic hydrogen by the

electron-donating methyl group increases the C=C bond length which is in agreement with the view of enhancing of the conjugation effect, but simultaneous increasing of C-N bond length is against this view. Similar trends were calculated by ab initio HF/6-31G* and DFT B3LYP/6-31G* calculations [12] and measured by electron diffraction [18,20] for C=O and C-N bonds in trans Nmethylformamide and trans N-methylacetamide. This might be due to steric effect as the methyl group is bulkier that hydrogen. However, substitution of an amino hydrogen by the electrondonating methyl group enhance the conjugation effect and a slight increase in the C=C bond lengths is accompanied by a slight decrease in the =C-N bond lengths. The same conclusion was made for aminomethylene propanedinitrile and its N-methyl derivatives [4] studied earlier, and was also calculated for structurally similar formamide and trans N-methylformamide and for acetamide and trans N-methylacetamide from ab initio HF/6-31G* and DFT B3LYP/6-31G* calculations [12]. These results are in agreement with the bond lengths from electron diffraction for formamide [16,17], trans N-methylformamide [18], acetamide [19] and *trans N*-methylacetamide [20]. The substitution of the second amino hydrogen by methyl group in N.N-dimethylformamide leads to further increase of the C=C bond length and also to the increasing of the =C-N bond length probably is due to steric effects of the bulky methyl group [12,21]. Then, the same result is not surprising for DMAE, where the steric effects due to olefinic methyl group are much higher. The tendency of forming a planar structure of the amino group with a higher degree of conjugation has also been discussed [4]. The repulsion steric effects of the methyl groups affect this tendency and therefore the calculated non-planar structure of DMAE with the three methyl groups is comprehensible.

4.2. Conformational energy

The conformational energies of MAE calculated by the all methods are at least three times higher than the experimental value determined from NMR spectra. Such high difference may be attributed to possible

Table 10				
Comparison of observed and	l calculated	vibrational	frequencies f	for DMAE

No.	Fundamental ^a	Observed ^b	Ab initio	Scaled ^c	PED^d
ν_1	CH ₃ asym stretch	3020	3340	3056	88 (C)CH ₃ as
ν_2	CH ₃ asym stretch	2989	3331	3047	87 (N)CH ₃ as
ν_3	CH ₃ asym stretch	2989	3329	3045	94 (N)CH ₃ as
ν_4	CH ₃ asym stretch	2975	3284	3004	95 (C)CH ₃ as
ν_5	CH ₃ asym stretch	2975	3280	3000	94 (N)CH ₃ as
ν_6	CH ₃ asym stretch	2951	3265	2986	83 (N)CH ₃ as
ν_7	CH ₃ sym stretch	2941	3206	2933	78 (N)CH ₃ ss
ν_8	CH ₃ sym stretch	2941	3205	2932	82 (N)CH ₃ ss
ν_9	CH ₃ sym stretch	2922	3181	2910	79 (N)CH ₃ ss
ν_{10}	C=N stretch	2209	2584	2210	89 C≡N s
ν_{11}	$C \equiv N$ stretch	2191	2575	2205	88 C \equiv N s
ν_{12}	C=C stretch	1585	1716	1573	41 C=C s, 34 C-N s
ν_{13}	C–N stretch	1551	1645	1504	13 C-N s, 20 C=C s, 12 C-CH ₃ s
ν_{14}	CH ₃ asym bend	1471	1621	1475	56 (N)CH ₃ aδ. 14 (C)CH ₃ aδ
ν_{15}	CH_3 asym bend	1471	1618	1472	74 (N)CH ₃ aδ
ν_{16}	CH_3 asym bend	1453	1610	1464	50 (N)CH ₃ aδ. 23 (C)CH ₃ aδ
ν_{17}	CH_3 asymber	1453	1608	1462	$74 (N)CH_3 a\delta$
ν_{19}	CH ₃ asym bend	1430	1592	1448	32 (C)CH ₃ aδ. 17 (N)CH ₃ aδ
ν_{10}	CH_3 asym bend	1424	1580	1437	51 (C)CH ₃ aδ. 21 (N)CH ₃ sδ
ν_{20}	CH_2 sym bend	1415	1569	1428	64 (N)CH ₂ sδ
V 20	CH ₂ sym bend	1383	1563	1424	$62 (N)CH_2 s\delta$
V 21	CH_2 sym bend	1378	1527	1389	84 (C)CH ₂ sδ
V 22	NC_2 asym stretch	1264	1409	1289	40 NC_2 as $17 \text{ C}=\text{CN} \delta$. 14 NC_2 ro
ν_{23}	CC_2 asym stretch	1220	1350	1233	26 CC_2 as 16 NC ₂ as 19
- 24			1000	1200	(N)CH ₃ ro
ν_{25}	CH ₃ rock	1158	1263	1153	28 (N)CH ₃ ro, 34 CC ₂ as
ν_{26}	CH ₃ rock	1158	1251	1138	100 (N)CH ₃ ro
ν_{27}	CH ₃ rock	1099	1218	1108	89 (N)CH ₃ ro
ν_{28}	CH ₃ rock	1086	1181	1076	50 (N)CH ₃ ro
ν_{29}	CH ₃ rock	1064	1161	1060	33 (C)CH ₃ ro, 20 NC ₂ as
ν_{30}	CH ₃ rock	1050	1142	1043	63 (C)CH ₃ ro
ν_{31}	C-CH ₃ stretch	1019	1108	1015	22 C-CH ₃ s, 21 NC ₂ ss, 14 (C)CH ₂ ro
	NC sym stratch	830	016	840	48 NC ss 13 CC ss 14
V 32	ive ₂ sym stretch	037	510	040	(C)CH ro
	C $C = N$ sym head	617	734	670	$20 CC = N s \delta 35 CC was 41 C$
V ₃₃	C-C-N sym bend	042	734	070	29 CC-IN S0, 55 CC ₂ wa, 41 C-
	CC deformation	621	604	625	34 CC = 8 30 CC = N s 8 17
V 34	CC_2 deformation	021	0)4	025	$C_{1} = \frac{1}{2} = \frac{1}{2$
	CC aum stratsh	617	670	615	10 CC as $24 C$ CH a
V 35	=C CH was	545	608	553	$19 CC_2 SS, 24 C-CH_3 S$ $34 C CH was 30 CC=N s\delta$
V ₃₆	$-C-CH_3$ wag	525	586	531	$15 CC=N_{3} \& 17 CC_{10} = 13$
ν_{37}	C-C-iv asym bend	525	580	551	$\frac{15 \text{ CC}-N \text{ ab}}{\text{NC}_2 \text{ b}}$
ν_{38}	C−C≡N asym bend	470	537	475	84 CC \equiv N a δ ,6C $=$ C τ
ν_{39}	C=C - N bend	449	493	442	$20 \text{ C}=\text{CN } \delta$, $26 \text{ NC}_2 \delta$, $10 \text{ NC}_2 \text{ ro}$
ν_{40}	NC ₂ deformation	432	467	426	19 NC ₂ δ , 24 NC ₂ ro, 26 C–
	-C CII	122	441	402	CH_3 ro
ν_{41}	=C – CH ₃ rock	432	441	402	$52=U-UH_3$ to
ν_{42}	NC ₂ fock	311	341	311	24 NC ₂ ro, 28 C=UN δ
ν_{43}	NC_2 wag		213	200	$\delta \delta INC_2$ Wa
ν_{44}	$N-CH_3$ torsion		241	224	$9/N-CH_3\tau$
ν_{45}	$C-CH_3$ torsion		227	211	82 C–CH ₃ τ

No.	Fundamental ^a	Observed ^b	Ab initio	Scaled ^c	PED^d
ν_{46}	CC ₂ wag	163	197	181	33 CC ₂ wa, 12 CC≡N sδ, 33 C− N τ
$ u_{47} $	CC ₂ rock	163	182	166	26 CC ₂ ro, 16 CC≡N aδ, 22 C− CH ₃ τ
ν_{48}	C−C≡N sym bend	163	171	153	48 CC \equiv N s δ , 40 CC ₂ δ
ν_{49}	N-CH ₃ torsion		145	135	121 N–CH ₃ τ
ν_{50}	=C – N torsion	85	100	93	103 C–N τ
ν_{51}	C=C torsion	73	67	62	90 C=C τ

Table 10 (continued)

^a Approximate description taking into account also the comparison of the spectra of all three samples.

^b Observed frequencies are from liquid if available.

^c Calculated using scaling factors mentioned in the text.

^d Potential energy distribution for scaled frequencies.

interactions of the highly polar MAE molecule with the polar solvents (DMSO) used for the experimental energy determination compared with the isolated molecule in the calculations. In difference with the previous calculations for aminomethylene propanedinitrile and its N-methyl derivatives [4], slightly better results are given in the semi-empirical methods. As has been already mentioned the anti conformer of MAE is destabilized by the olefinic methyl group and the less energy difference between conformers can be expected. Measured energy difference really decrease from the value $3.4 \pm 1.1 \text{ kJ mol}^{-1}$ for (methylamino)methylene propanedinitrile [4] to the value $1.9 \pm 1.3 \text{ kJ mol}^{-1}$ for MAE. This trend is reflected by all the semi-empirical methods, but not by the ab initio method at HF level and probably calculations at MP2 level are necessary.

4.3. NMR spectra

The general behaviour is comparable to the nonmethylated at C₂ compounds reported in Ref. [4]. The chemical shifts of C₂ are changed downfield by approximately 10 ppm as expected by the methyl group substitution. For the *N*-monomethylated compound MAE two conformers *anti* and *syn* exist, as well. The assignment of NMR spectra to the conformers results from the vicinal coupling constants values (Table 4): *trans* couplings are about twice as large as the *cis* couplings in all cases. From the concentration ratio *anti:syn* 70:30 at room temperature the value of ca. 2.1 kJ mol⁻¹ for the Gibbs free enthalpy can be calculated. This value is by 1.4 kJ mol⁻¹ lower than for the similar molecules of (methylamino)methylene propanedinitrile [4]. Introducing the methyl group at C2 atom decreases the anti:syn ratio, the anti conformer population becomes less preferred. In contrast to (dimethylamino)methylene propanedinitrile [4], at the same temperature, we observed only one (collapsed) signal for C₄ and C₆ of the DMAE. The chemical shift of 42.8 ppm nearly equals the mean value of the different signals at 37.8 and 46.8 ppm of (dimethylamino)methylene propanedinitrile. From this fact a decrease of the rotational barrier around the C2-N3 axis or, in other words, decrease of the double bond character of this bond by methylation at C_2 is to be concluded. Observed free rotation of the DMAE dimethylamino group in comparison with the hindered rotation of the same group in (dimethylamino)methylene propanedinitrile confirm the calculated non-planar structure of the $C=C-NC_2$ moiety. Non-planar structure means decreasing of the conjugation and lowering of the rotation barrier.

The proton NMR spectra obtained at 300 MHz also reflect the hindrance of rotational motion around the C_2-N_3 axis. AE has two broadened signals of H₄ and H₆. The temperature dependence of the MAE conformer mixture spectra results in an activation energy of 75.8 kJ mol⁻¹ for the *syn-anti* exchange calculated by the coalescence temperature (350 K) of the *N*-methyl proton signals. In DMAE the *N*-methyl signals collapse at room temperature in analogy to the ¹³C NMR spectra. Additionally, the

temperature dependence of DMAE in deuterated acetone solution was measured. Spectra revealed that coalescence temperature is 283 K and lowering the temperature leads to splitting of *N*-methyl signals. The proton chemical shifts in acetone at 273 K are 3.430 and 3.305 ppm for *N*-dimethyl and 2.320 ppm for olefinic protons. From the chemical shift difference and coalescence temperature the free standard enthalpy of activation 58.7 kJ mol⁻¹ was calculated.

4.4. Vibrational spectra

The N–H stretching modes are those with the highest wave numbers and, therefore, their assignment in the vibrational spectra for AE and MAE is straightforward. A doublet band structure of these vibrational modes in the solid and solution spectra has been discussed [4]. The bands in the C–H frequency region belong only to the CH_3 stretching modes. Their assignment is not clear without additional isotopic studies and is based only on the normal coordinate calculations.

The C \equiv N stretching modes were found at about 5–10 cm⁻¹ lower than for the aminomethylene propanedinitrile and its *N*-methyl derivatives studied earlier [4]. The wave number downshifts correspond with the very slight decrease of the multiple character of these bonds due to increasing of the conjugation after substitution of the olefinic hydrogen by the electrondonating methyl group.

The C=C stretching mode frequency 1662 cm^{-1} for the previously studied aminomethylene propanedinitrile, 1648 and 1630 cm⁻¹ for anti and syn conformers of (methylamino)methylene propanedinitrile and 1644 cm⁻¹ for (dimethylamino)methylene propanedinitrile were found [4]. Highest frequencies in this region above 1500 cm^{-1} are 1653 and 1554 cm^{-1} for AE, 1602 and 1577 cm⁻¹ for MAE and 1585 and 1551 cm⁻¹ for DMAE. According to the normal coordinate calculations the C=C stretching mode is mixed with the NH₂ scissoring mode for AE, with the N-H rocking mode for MAE and with the C-N stretching mode for DMAE. Therefore, the assignment of the C=C stretching mode to the band with the highest frequency is not straightforward. Nevertheless, the highest mentioned frequencies are lower than for the earlier studied compounds [4] and confirm the calculated slight decrease of the double bond character of the C=C bond in studied molecules after substitution of the olefinic hydrogen by the electron-donating methyl group. The C-N stretching mode frequencies for the earlier studied aminomethylene propanedinitrile, (methylamino)methylene propanedinitrile and (dimethylamino)methylene propanedinitrile were assigned at 1329, 1337 and 1408 cm^{-1} , respectively [4]. For compounds studied in this article, increasing of the C-N stretching mode frequency from 1439 cm^{-1} for AE to 1551 cm^{-1} for DMAE can be concluded. Similar frequency upshift of the C-N stretching mode (amide III mode) was observed after substitution of the carbonyl hydrogen by the methyl group for formamide and acetamide, and trans N-methylformamide and trans N-methylacetamide [22].

In-plane vibrational modes (scissoring and rocking) of the amino groups -NH2 and -NH are in the expected regions [22]. According to the calculated PED, the bands at 548 cm^{-1} for AE and 522 cm^{-1} for MAE were assigned as the non-planar wagging modes of the -NH2 and -NH groups, respectively. However, common features of both the 625 cm^{-1} for AE and 707 (or 679) cm⁻¹ for MAE bands—strong and broad bands in IR spectra and absence in Raman spectra, frequency downshift in the solution spectra-and the fact that a band of such character is not present in this region in the vibrational spectra of DMAE indicate the assignment of these bands amino groups. Also, a calculated higher to frequency for the NH₂ torsional mode compared with the NH₂ wagging mode is characteristic for planar amides rather than for non-planar aliphatic or aromatic amines where the NH2 wagging mode is in the region $700-850 \text{ cm}^{-1}$ [22]. This means that the measured lower frequency of 625 cm⁻¹ for the NH₂ out-of-plane mode support the planar structure of the amino group.

As for the aminomethylne propanedinitrile and its *N*-methyl derivatives [4] studied earlier, the normal coordinate calculations indicate again that each of the four C–C=N linear bending modes is mixed with one of the four deformation modes of the =CC₂ group. The CC₂ scissor is mixed with the inplane symmetric linear bending mode of both CC=N groups, and the CC₂ rock is mixed with the in-plane

CC=N asymmetric linear bending mode. The CC₂ wag is mixed with the out-of-plane symmetric linear bending mode of both CC=N groups. The CC₂ twist for a non-planar CC_2 structure or the C=C torsional mode for a planar=CC₂ structure is mixed with the out-of-plane asymmetric CC=N linear bending mode. In each mentioned pairs one mode should occur between 400 and 600 cm⁻¹ and the other between 100 and 300 cm⁻¹.

The out-of-plane asymmetric CC=N linear bending appears as the most localized mode according to the PED, and therefore its assignment is the most straightforward among the bands in the very narrow region 464–470 cm⁻¹ for all the three samples. The corresponding C=C torsional mode is due to substitution of the olefinic hydrogen shift down to 100 cm⁻¹.

The CC₂ scissoring and the in-plane symmetric CC \equiv N linear bending modes are both highly mixed as previously reported for 1,1-dicyanocyclopropane [23], 1,1-dicyanocyclobutane [24] and carbonyl cyanide [25]. Based on these results, we assigned the CC₂ scissoring mode in the high frequency region 605–621 cm⁻¹ and the corresponding CC \equiv N linear bend in the low frequency range.

The two remaining CC^2 modes (rocking and wagging), although mixed with the mentioned $CC \equiv N$ modes, should occur in the low frequency region. The $CC \equiv N$ bending modes were assigned in the regions 521-533 cm⁻¹ (the in-plane asymmetric linear bend) and 642-707 cm⁻¹ (the out-of-plane symmetric linear bend), respectively. It is necessary to note that the last bending mode mixed with the CC_2 wagging mode was calculated at about 100 cm⁻¹ higher than for the related compounds mentioned [4,23-25]; therefore, its interchanging with the $-NH_2$ and -NH wagging mode for AE and MAE, respectively, is plausible.

The C=C-N bending mode was assigned for all the three samples to a band with very similar character in the narrow frequency interval 438-449 cm⁻¹.

The assignment of the deformation modes and especially of the torsional modes below 250 cm^{-1} is very tentative because spectral data from the fluid phases are missing in this region and many lattice modes for AE and MAE are present in the solid phase spectra.

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