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1-(Arylchloromethyl)pyridinium chlorides. Investigation by X-ray single crystal diffraction and semiempirical (PM3, AM1, MNDO) calculations

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Abstract

The molecular structures of 1-[chloro(2-methoxyphenyl)methyl]pyridinium chloride and 1-[chloro(3-nitrophenyl)methyl]pyridinium chloride were studied by X-ray single crystal diffraction and semiempirical calculations (PM3, AM1, and MNDO) in comparison with model compounds to give a deeper insight into reactivity of these pyridinium salts. Feasibility of the nucleophilic substitution of the chlorine atom in such cations finds its explanation in a relatively strong exocyclic N-C bond, which suppresses the substitution of the pyridine ring system. PM3 was found to be sufficiently accurate to predict the structure of such cations correctly. For both cations, nonsymmetric conformations were observed in crystalline phase being mainly determined by the chlorine substituents at the exocylic C_{α} atoms. The acidity of the methylene hydrogens promotes the formation of intermolecular C-H…Cl⁻ hydrogen bonds in both compounds. © 1998 Elsevier Science B.V.

1. Introduction

Recently, a group of Belgian and German coworkers developed new synthetic pathways to numerous nitrogen containing heterocyclic compounds: N-(1haloalkyl)– and N-[1-halo(aryl)methyl]azinium halides [1]. Prepared *in situ*, they were subjected to substitution reactions in which the halogen atom was replaced by nitrogen nucleophiles [2,3]. Our mutual interest in the chemistry of pyridinium salts led to this structural study of the title compounds. The aim of this investigation is to get insight into the steric demand of the substituents around the reaction center, the exocyclic C_{α} atom. This steric effect is supposed to correlate with reactions rates of such salts. Further, it seemed to be interesting to trace down the mutual influence of the constituents of these cations by comparing suitable model compounds (the corresponding substituted benzenes, pyridinium halides, and benzyl halides). Thus, the structure of 1-[chloro(2-methoxyphenyl)methyl]pyridinium chloride (1) and 1-[chloro(3-nitrophenyl)methyl]pyridinium chloride (2) was determined by

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X-ray single crystal diffraction. The resulting structural data can serve as the fundament for semiempirical calculations (using the PM3, AM1, and MNDO hamiltonians) in order to assess the most suitable method to predict structures and reactivity pattern for the class of pyridinium salts discussed here. The cations 3-5 are model cations which have been included in the calculational part, *vide infra* (Scheme 1).

2. Experimental

¹H NMR spectra were obtained on a Varian EM 360-L spectrometer and IR spectra on a Perkin-Elmer 577 spectrometer. Melting points (uncorrected) were determined on a hot-stage microscope. Elemental analyses were performed by the Station de Haute-Belgique (Libramont-Chevigny, Belgium).

2.1. Synthesis

1-[Chloro (2-methoxyphenyl)methyl] pyridinium chloride (1) and 1-[chloro(3-nitrophenyl)methyl]pyridinium chloride (2) were prepared from thionyl chloride, pyridine and the corresponding aldehyde following the procedure described in [4]. These compounds have been described in the literature [5,6] but have not been isolated before the present study.

2.1.1. Preparation of the pyridinium salts—general procedure

A solution of thionyl chloride (0.9 ml; 12 mmol) in dichloromethane (12 ml) was cooled to 0°C. Pyridine

(1.0 ml; 12 mmol) and the aldehyde (10 mmol) were added successively and the mixture was allowed to warm to room temperature for 15 min.

2.1.2. 1-[Chloro(2-methoxyphenyl)methyl]pyridinium chloride [5]

Analytically pure samples of the product were obtained by slow evaporation of the solvent (dichloro-methane).

¹H NMR (D₂O/external TMS): 4.3 (s; 3H; OCH₃); 7.6–8.2 (m; 4H; Ar); 8.6 (s; 1H; CHCl); 8.7 (m; 2H; H³ and H⁵ pyr); 9.2 (t; J = 8 Hz; 1H; H⁴ pyr); 9.8 (d; J = 5 Hz; 2H; H² and H⁶ pyr) ppm. IR (KBr): 3010; 2930; 1600; 1420 cm⁻¹. M.p.: 225–227°C $C_{13}H_{13}NOCl_2$ (270.16) Anai. Calcd. C: 57.80; H: 4.85; N: 5.19. Found C: 57.87; H 5.06; N: 5.22.

2.1.3. 1-[Chloro(3-nitrophenyl)methyl]pyridinium chloride [6]

The precipitate was filtrated and recrystallized from acetonitrile.

¹H NMR (D₂O/external TMS): 8.2 (t; J = 7 Hz; 1H; H⁵ Ar); 8.3–8.9 (m; 6H; H², H⁴ and H⁶ Ar; CHCl; H³ and H⁵ pyr); 9.2 (t; J = 8 Hz; 1H; H⁴ pyr); 9.7 (d; J = 5 Hz; 2H; H² and H⁶ pyr) ppm. IR (KBr): 3020; 2920; 2860; 1620; 1520; 1490; 1470; 1350; 1150 cm⁻¹. M.p.: 191–194°C. $C_{12}H_{10}N_2O_2Cl_2$ (285.13)

Table 1	
Summary	of crystallographic data

	1	2	
Formula	C ₁₃ H ₁₃ NOC1 ⁺ .Cl ⁻	$C_{12}H_{10}N_2O_2Cl^+.Cl^-$	
Formula wt.	270.16	285.13	
M.p. (°C)	225-227	191-194	
Space group	C2/c	C2/c	
a (Å)	8.520(1)	14.715(5)	
b (Å)	14.576(2)	7.972(2)	
c (Å)	20.806(3)	22.187(7)	
β (deg)	97.06(1)	94.08(3)	
Z	8	8	
V (Å ³)	2564.1	2596.1	
$\mu_{\text{cale.}}$ (cm ⁻¹)	4.89	4.94	
$d_{\text{calc.}}$ (g cm ⁻³)	1.40	1.46	
F(000)	1120	1168	
2θ range	3.0-60	3.0-54	
Scan type	$\omega/(5/3\theta)$	$\omega/(5/3\theta)$	
Reflect. obs. $F^2 \ge 3\sigma(F^2)$	2112	1245	
No. Parameters	206	203	
R	0.034	0.043	
wR	0.049	0.059	

Anal. Calcd. C: 50.55; H: 3.54; N: 9.82. Found C: 50.68; H: 3.48; N: 9.64.

2.2. X-ray structure determination

The X-ray data were measured for crystals 1 and 2 on a CAD4 Enraf–Nonius automatic diffractometer using graphite monochromated Mo K_{α} radiation. The relevant experimental parameters and crystal structure data are given in Table 1. Corrections for Lorentz and polarization effects were applied. The stability of the crystals and that of the experimental conditions were checked every hour using two control reflections, while the orientation was monitored every 200 reflections by centering two standards. Neither decay nor absorption corrections were necessary.

The structures were solved by direct methods with the program MULTAN; E map revealed all the nonhydrogen atoms and their positions were refined by the full-matrix least-squares method with anisotropic temperature factors. All hydrogen atoms were located from difference Fourier syntheses and their positions were refined isotropically.

All calculations were carried out on a PDP 11/23 computer using SDP programs.

Table 2

Selected bond lengths (Å) in the molecules of 1-[chloro(2-methoxyphenyl)methyl]pyridinium chloride (1) and 1-[chloro(3-nitrophenyl)-methyl]pyridinium chloride (2)

Bond	1	2	Bond	1	2	
CI1-C1	1.782(2)	1.772(4)	C3-C4	1.375(3)	1.365(7)	
01-N		1.198(4)	C4-C5	1.383(3)	1.346(6)	
02-N	_	1.229(4)	C5-C6	1.370(3)	1.354(5)	
N-C9		1.494(5)	C7-C8	1.395(3)	1.379(5)	
N1-C1	1.501(2)	1.510(5)	C7-C12	1.380(3)	1.377(5)	
N1-C2	1.347(2)	1.356(5)	C8-C9	1.386(3)	1.376(5)	
N1-C6	1.346(2)	1.330(5)	C9-C10	1.389(3)	1.373(5)	
C1-C7	1.500(2)	1.512(5)	C10-C11	1.373(4)	1.370(6)	
C2-C3	1.374(3)	1.376(6)	C11-C12	1.385(3)	1.379(6)	
O-C8	1.366(2)		O-C13	1.418(3)		

Table 3

Angle	1	2	Angle	1	2	
01NO2		124.5(4)	C4C5C6	119.1(2)	120.5(4)	
O1NC9		117.9(4)	N1C6C5	120.0(2)	120.0(4)	
O2NC9		117.5(4)	C1C7C8	116.3(2)	116.0(3)	
C1N1C2	118.5(2)	114.7(3)	C1C7C12	124.9(2)	123.7(3)	
CINIC6	119.8(1)	123.8(3)	C8C7C12	118.8(2)	120.3(3)	
C2N1C6	121.8(2)	121.4(3)	C7C8C9	120.9(2)	117.9(3)	
CHCINI	107.0(1)	109.3(3)	NC9C8	_	118.7(3)	
CIICIC7	113.8(1)	111.4(3)	NC9C10		118.5(4)	
NICIC7	111.8(1)	111.6(3)	C8C9C10	119.2(2)	122.7(4)	
N1C2C3	119.6(2)	118.7(4)	C9C10C11	120.1(2)	118.5(4)	
C2C3C4	119.5(2)	119.6(4)	C10C11C12	120.4(2)	120.1(4)	
C3C4C5	119.9(2)	119.8(4)	C7C12C11	120.5(2)	120.4(4)	
C8OC13	117.9(2)		OC8C7	114.5(2)		

Selected valence angles (deg.) in the molecules of 1-[chloro(2-methoxyphenyl)methyl]pyridinium chloride (1) and 1-[chloro(3-nitrophenyl)-methyl]pyridinium chloride (2)

Bond lengths and valence angles are given in Tables 2-3. In Table 4 we present torsional angles which we believe are relevant to the discussion. Molecular structures are given in Figs. 1 and 2.

3. Discussion

3.1. Geometry of the pyridinium ring

The average length (1.35 Å) of the cyclic N-C bonds is the same in our molecules 1, 2 and in more simple compounds 3 and 5, as determined by X-ray single crystal diffraction [7], and is very close to its value in pyridine. The structure of the latter was determined by a complex of methods including gas electron diffraction, microwave spectroscopy, vibrational spectroscopy and ab initio calculations at 4-21G level [8]. The substitution at nitrogen in compounds 1-3 and 5 enlarges endocyclic C-N-C valence angle to 121° (average value) in comparison to 116.1° in gaseous pyridine [8]. To assess the reliability of the three 'popular' semiempirical methods PM3[9], AM1[10], and MNDO [11] in describing structures in this series of cations with acceptable accuracy, the species 1-5 have been calculated (Tables 5-7). All cations have been optimized without symmetry restrictions using the MOPAC6/PC program package [12]. The counter ions (Cl⁻) were not included in these gas phase calculations.

The results indicate that the PM3 calculated values of the free cations agree best with the experimental data. Most features of the conformational properties are reproduced by this method too.

To understand structural changes (especially for the bond lengths) we choose *N*-methylpyridinium to be the reference cation.

All the N1-C1 values are within a relatively narrow

Table 4

Selected torsional angles (deg.) in the molecules of 1-[chloro(2-methoxyphenyl)methyl]pyridinium chloride (1) and 1-[chloro(3-nitrophenyl)-methyl]pyridinium chloride (2)

Angle	1	2	Angle	1	2	
O1NC9C8			CliC1C7C8	-163.2	-128.6	
C2N1C1C11	109.9	137.3	CI1C1C7C12	14.2	50.5	
C2N1C1C7	-124.8	-99.1	N1C1C7C8	75.4	108.9	
C2N1C1H1	-1.0	16.8	N1C1C7C12	-107.2	-72.0	
C6N1C1Cl1	-70.3	-45.8	H1C1C7C8	-46.2	-9.3	
C6N1C1C7	55.0	77.8	HICIC7C12	131.2	169.9	
C6N1C1H1	178.8	-166.4	C7C8OC13	167.2	—	



Fig. 1. PLUTON drawing of cation 1.

interval, compared with our findings for cations in which, for example, an oxygen atom is bound to the C1 atom [13]. Such substituents cause a significant elongation of that bond. This observation was explained with the influence of the anomeric effect (or the negative hyperconjugation). This effect obviously is not expressed in the chloro derivatives 1, 2, and 4, as the N1-C1 bond lengths remain almost constant and come out to be only slightly elongated compared with that of the standard cation 5. Thus, nucleophilic substitution of the pyridinium moiety will be suppressed in favor of the replacement of the Cl atom. This is in agreement with our previously published experimental observations.

Exchange of one H atom of the methyl group of **5** by the phenyl group to give *N*-benzylpyridinium causes a slight elongation of the N1-C1 bond (from 1.481 to 1.502 Å; PM3 results) and therefore is of more influence on structural changes than the analogous H to Cl exchange: the latter (conversion of **5** to **4**) does not affect the N1-C1 bond length to a significant extent. Further, not unexpectedly, the



Fig. 2. PLUTON drawing of cation 2.

Cation	Bond	PM3	AM1	MNDO	X-ray	
1	N1-C1	1.514	1.489	1.514	1.501(2)	
	CI1-C1	1.785	1.766	1.805	1.782(2)	
2	N1-C1	1.513	1.487	1.511	1.510(2)	
	Cl1-C1	1.780	1.764	1.798	1.772(4)	
3	N1-C1	1.502	1.478	1.520	1.495(5)	
4	N1-C1	1.489	1.465	1.494		
	Cl1-Cl	1.772	1.746	1.785		
5	N1-C1	1.481	1.456	1.500		

Table 5 Comparison of some calculated and experimentally determined bond lengths (Å)

substituents at the benzene ring (cations 1 and 2) do not cause significant structural changes of the central N1-C1-C11 moiety, too.

3.2. Geometry of methoxybenzene moiety and orientation of methoxy-group

Geometry of the benzene ring in compound 1 is close to unsubstituted benzene [14]. Carbon-carbon bond lengths lie in the interval of 1.373–1.395 Å and endocylic valence angles are equal to 118.9– 120.9°. Methoxy-group is twisted from the plane of the benzene ring by 13.5°, being *anti*-oriented respective to the *N*-chloromethylpyridinium substituent in the *ortho*-position. According to the statistical data on anisoles (Ar-OCH3) [15,16] derived from the Cambridge Structural Database, methoxygroup usually adopts planar conformation with

 $\angle C_{ar}$ - C_{ar} -O-Me < 10° in the molecules containing either meta or para-substituents. This conformation is also preserved when the anisole derivative is substituted in one of the ortho-positions but perpendicular conformation is realized in di-ortho-substituted molecules. Internal rotation of methoxy-group is accompanied by regular geometrical changes. Valence angle at oxygen and O-C_{ar}-C_{ar} angle tend to change so that to provide maximal distance between the methyl group and ortho-substituent syn to it. So the values of C_{ar}-O-Me angle change from 124.8° in our compound to 115° typical to perpendicular orientation. Average $O-C(sp^2)$ and O-Me bond lengths are equal to 1.367 and 1.424 Å respectively [16]. Comparing the data obtained for compound 1 containing ortho-substituted anisole moiety it should be noted that it is in a good accordance with the structural trends established in [15,16].

Table 6

Comparison of some calculated and experimentally determined bond angles (deg.) in the molecules of 1-[chloro(2-methoxyphenyl)methyl]pyridinium chloride (1) and 1-[chloro(3-nitrophenyl)methyl]pyridinium chloride (2)

Cation	Angle	PM3	AM1	MNDO	X-ray
1	C1N1C2	119.7	120.1	119.2	118.5(2)
	N1C1C7	110.0	111.6	112.6	111.8(1)
	CIC1N1	107.6	110.0	105.3	107.0(1)
	CIC1C7	112.1	113.0	116.0	113.8(1)
	C8OC13	117.7	116.4	124.3	117.9(2)
	OC8C7	115.3	113.0	116.1	114.5(2)
2	CINIC2	119.5	119.7	119.3	114.7(3)
	NICIC7	110.5	112.1	112.1	111.6(3)
	CIC1N1	108.8	110.3	106.4	109.3(3)
	CIC1C7	111.7	112.6	115.7	111.4(3)
	NC9C10	120.3	119.9	119.4	118.5(4)
	O1NC9	117.8	118.4	118.1	118.7(3)

Cation	Angle	PM3	AM1	MNDO	X-ray	
1	C2N1C1Cl1	+114.9	+108.9	+102.6	+109.9	
	C2N1C1C7	-123.8	-124.8	-130.3	-124.8	
	N1C1C7C8	+86.8	+87.0	+75.5	+75.4	
	C7C8OC13	+167.1	+169.9	+159.3	+167.1	
2	C2N1C1CI1	+131.4	+98.4	+108.4	+137.3	
	C2N1C1C7	-105.7	-134.8	-124.1	-99.1	
	N1C1C7C8	+89.6	+87.7	+77.0	+108.9	
	O1NC9C8	-13.6	-3.6	-68.9	9.8	

Comparison of some calculated and experimentally determined torsional angles (deg.) in the molecules of 1-[chloro(2-methoxyphenyl)methyl]pyridinium chloride (1) and 1-[chloro(3-nitrophenyl)methyl]pyridinium chloride (2)

3.3. Geometry of nitrobenzyl moiety

Table 7

According to the X-ray single crystal diffraction study the molecule of nitrobenzene has the following geometry: r(C8 - C9) = 1.37, r(C10 - C11) = 1.39, r(C11 - C12) = 1.40, r(C9 - N) = 1.49, r(N - O) = $1.20 \text{ Å}, \angle C8 - C9 - C10 = 124.8^{\circ}, \angle O1 - N - O2 =$ $123.8^{\circ}, \angle O1 - N - C9 - C8 = 1.9^{\circ}$ [17]. Electron diffraction data for nitrobenzene are in full accordance with the data for crystalline phase except for the orientation of the nitro-group with the corresponding torsional angle being equal to 13.2° [18]. Nonplanarity of this molecule in gaseous phase is probably determined by the torsional vibrations of the nitro-group. According to ED data, the rotational barrier of the nitro-group V_2 is equal 17 \pm 4 kJ/mol [18], this value being consistent with the results obtained by Raman spectroscopy (13.6 kJ/mol) [19]. It should be mentioned that MO calculations at the STO-3G level with geometry optimization give a value of the barrier to rotation in nitrobenzene, 20.8 kJ/mol [20], which is closer to the above experimental result than any of the values obtained by

adding polarization functions on the non-hydrogen atoms (e.g. value V_2 31.8 kJ/mol obtained by using the GAUSSIAN 82 program with gradient optimization with the 6-31G basis set [18]). In compound **2**, studied by us, nitro-group is remote from *N*-chloromethylpyridinium substituent with the chlorine atom being in *anti*-position respective to nitro-group. Thus, the geometrical parameters (Tables 2 and 3) obtained for compound **2** are in a good accordance with the data obtained for nitrobenzene.

3.4. Conformation of chlorobenzyl moiety

The general conformational trend observed for monohalo- and cyanobenzyls that do not bear *ortho*substituents is the eclipsed orientation of one of the methylene C–H bonds by the benzene plane [21]. The number of the halogen atoms being increased or other substituents being introduced into benzene ring, its plane is in eclipsed position to the less bulky geminal bond. In case all three R substituents in the fragment R_3C -Ar are bulky, orthogonal conformation is observed. The results



obtained by us for 2 are in a good accordance with this trend: the C1-H1 bond is nearly coplanar to the metanitrobenzene plane ($\angle C8 - C7 - C1 - H1 = -9.3^{\circ}$). Pyridinium ring in 2 is also close to the eclipse orientation towards the geminal C-H bond (\angle C2-N1 - C1 - H1 = 16.8°). In molecule 1 only pyridinium ring, which may be treated as structural analogue of the benzene, eclipses the geminal C-H bond, while the benzene ring is coplanar to C–Cl bond (\angle Cl – Cl – $C7 - C12 = 14.2^{\circ}$). When an *ortho*-substituent is introduced to the benzene ring of monohalo- or monocyanobenzyls, an equilibrium between two conformers is usually observed in solutions with syn and anti-orientations of C-Hlg (CN) and ortho-substituent in the ring (e.g. [22]). In the crystalline phase of compound 1 anti-conformation is observed ($\angle C8 - C7 - C1 - C1$ = -163.2°) with short intramolecular H12···Cl1 contact (2.67 Å) which may be interpreted as an intramolecular C-H···Cl bond with the following parameters: C12-H12 0.89 Å, H12...Cl1 2.67 Å, ∠C12-H12…Cl1 108°.

3.5. Mutual orientation of benzene and pyridinium rings

Considering the conformations of molecules 1–3, let us define torsional angles of rotation of the benzene ring as ϕ_b (C8-C7-C1-N) and of the pyridine ring as ϕ_p (C2-N-C1-C7) with $\phi_b = \phi_p = 0^\circ$ for planar conformation. For diphenylmethane derivatives two symmetric forms (C₂ and C_s) including planar ($\phi_b = \phi_p = 0^\circ$) and gable ($\phi_b = \phi_p = 90^\circ$) forms, as well as a variety of C₁ forms with $\phi_b \neq \phi_p$ are possible in general [23]. Similar conformations can be considered for compounds 1–3 (Scheme 2).

Two independent molecules in the unit cell of crystals **3** with $\phi_b = -111.3^\circ$, $\phi_p = 93.2^\circ$ and $\phi_b = 115.4^\circ$, $\phi_p = -88.2^\circ$ were found in [7], these two forms being identical due to the absence of substituents in the benzene and pyridine rings. For **1** and **2** we have found nonsymmetric conformations with the torsional angles $\phi_b = 75.3^\circ$, $\phi_p = -124.8^\circ$ and $\phi_b = 108.8^\circ$, $\phi_p = -99.1^\circ$ respectively. Slightly distorted helical conformations with $\phi = 50-70^\circ$ were observed for diphenylmethane and its derivatives substituted into *meta* and *para*-positions [23], which are the structural analogues of compounds **1**-**3**. For various *ortho*-substituted diphenylmethane derivatives

slightly distorted gable structures ($\phi = 80-85^{\circ}$) and perpendicular forms ($\phi_1 = 0-10^{\circ}$, $\phi_2 = 80-90^{\circ}$) were revealed [23]. The main conclusion which may be derived from the comparison of the mutual orientation of benzene and pyridine rings in 1 and 2 with the literature data is that the presence of chlorine at the methylene carbon atom is the major factor determining the conformations of molecules 1 and 2.

3.6. Short contacts between nonbonded atoms

Besides the intramolecular C-H···Cl hydrogen bonding in molecule 1, intermolecular C1-H···Cl⁻ short contacts are observed in both compounds studied, promoted by the acidity of the methylene hydrogen. The parameters of these short contacts meet the criteria of the X-C-H···Y⁻ hydrogen bond, where X is an electronegative atom or group and Y⁻ is a counter ion [24]. Compound 1: C1-H1···Cl⁻ 2.66 Å, C1···Cl⁻ 3.56 Å, \angle C1-H1···Cl⁻ 156°, compound 2: C1-H1···Cl⁻ 2.36 Å, C1···Cl⁻ 3.43 Å, \angle C1-H1···Cl⁻ 168°.

4. Conclusion

From this investigation we conclude that the feasibility of the nucleophilic substitution of the chloro atom in cations such as 1 and 2 finds its explanation in a relatively strong N1–C1 bond which suppresses the substitution of the pyridinium ring system. Especially the semiempirical PM3 method supports this assumption which was found to be sufficiently accurate for reliable calculations of cations containing a *N*-heteroaromatic ring system.

5. Supplementary material

Tables of positional parameters and equivalent isotropic thermal factors for crystals 1 and 2 are available from B. L. L. D. as Supplementary Publication number SUP 26591 (2 pages).

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References

- [1] E. Anders, J.G. Tropsch, Bull. Soc. Chim. Belg. 96 (1987) 719.
- [2] J.-J. Vanden Eynde, A. Mayence, A. Maquestiau, E. Anders, Synth. Commun. 22 (1992) 3141.
- [3] J.-J. Vanden Eynde, A. Mayence, A. Maquestiau, E. Anders, Bull. Soc. Chim. Belg. 102 (1993) 357.
- [4] A. Maquestiau, E. Anders, A. Mayence, J.-J. Vanden Eynde, Chem. Ber. 124 (1991) 2013.
- [5] J.-J. Vanden Eynde, J. Godin, A. Mayence, A. Maquestiau, E. Anders, Synthesis (1993) 867.
- [6] J.-J. Vanden Eynde, P. D'Orazio, A. Mayence, A. Maquestiau, E. Anders, Tetrahedron 48 (1992) 867.
- [7] E. Anders, J.G. Tropsch, E. Irmer, G.M. Sheldrick, Chem. Ber. 123 (1990) 321.
- [8] W. Pyckhout, N. Noremans, V. Alsenoy, H.J. Geise, D.W.H. Rankin, J. Mol. Struct. 156 (1987) 315.
- J.J.P. Stewart, J. Comput. Chem. 10 (1989) 36; E. Anders, R. Koch, P. Freunscht, J. Comput. Chem. 14 (1993) 1301.
- [10] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, J. Am. Chem. Soc. 107 (1985) 3902.
- [11] M.J.S. Dewar, W. Thiel, J. Am. Chem. Soc. 99 (1977) 4899.
- [12] R. Koch, B. Wiedel, QCMP 113, QCPE Bull., (1992), 12;

J.J.P. Stewart, QCPE 455. The MOPAC keywords 'PRECISE' and 'CHARGE = 1' were applied.

- [13] E. Anders, F. Markus, H. Meske, J. Tropsch, G. Maas, Chem. Ber. 120 (1987) 735.
- [14] A. J. Gordon, R. A. Ford. The Chemist's Companion, Wiley-Interscience, NY, 1972, p. 541.
- [15] S.C. Nyburg, C.H. Faerman, J. Mol. Struct. 140 (1986) 347.
- [16] W. Hummel, K. Huml, H.-B. Bürgi, Helv. Chim. Acta 71 (1988) 1291.
- [17] F. DiRienzo, A. Domenicano, Acta Cryst. B36 (1980) 586.
- [18] A. Domenicano, G. Schultz, I. Hargittai, M. Colapietro, G. Portalone, P. George, C.W. Bock, Struct. Chem. 1 (1990) 107.
- [19] L.A. Carreira, T.G. Towns, J. Mol. Struct. 41 (1977) 1.
- [20] S. Marriot, R.D. Topson, Austr. J. Chem. 39 (1986) 1157.
- [21] A.N. Vereschchagin, V.E. Kataev, A.A. Brediklin, A.P. Timosheva, G.I. Kovylyaeva, E.K. Kazakova, in: B.A. Arbuzov (Ed.), Conformational analysis of hydrocarbons and their derivatives, 'Nauka', Moscow, 1990, p. 296.
- [22] I.Yu. Strobykina, S.G. Vul'fson, V.E. Kataev, O.Yu. Butenko, A.N. Vereshchagin, Zh. Obshch. Khimii 58 (1988) 457.
- [23] J.C. Barnes, J.D. Paton, J.R.Damewood Jr., K. Mislow, J. Org. Chem. 23 (1981) 4975.
- [24] R. Gautam, R. Desiraju, Account Chem. Res. 24 (1991) 290.