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SCF-Perturbational Analysis of the *trans* Lone Pair Effect in Methylamine and Methanol

Vinzenz Bachler and Gottfried Olbrich

Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, Stiftstr. 34-36,
D-4330 Mülheim a.d. Ruhr, Federal Republic of Germany

The *trans* lone pair effect on the C—H bonds in methylamine and methanol has been analysed by means of CNDO/2 SCF perturbation theory using localised orbitals. The lone pair electrons are partially delocalized into the antibonding C—H orbital being *trans* orientated to the lone pair. This finding supports Hamlow's intuitive rationalization of the *trans* lone pair effect.

Key words: SCF-perturbation theory – *trans* effect – Orbital interaction scheme.

1. Introduction

A lone pair in a molecule influences profoundly the molecular conformation [1], bond properties [2], and reactivity [2]. The dependence of the C—H bond properties on *trans* oriented lone pairs became unequivocally apparent from McKean's investigations of individual C—H stretching frequencies [3]. In the gas phase infrared spectra of deuterated methylamine CHD_2NH_2 two bands at 2880 cm^{-1} and 2955 cm^{-1} are observed [4]; for deuterated methanol CHD_2OH frequencies at 2920 cm^{-1} and 2979 cm^{-1} [5] are identified. The lower frequencies have been assigned to C—H bonds which are located *trans* to the lone pair [4, 5]. The higher frequencies have been attributed to C—H bonds orientated *trans* to the N—H or O—H bond, respectively [4, 5]. A correlation of the individual C—H frequencies of various compounds with experimental bond lengths [3] and dissociation energies [3] supports nonequivalent methyl C—H bonds in methylamine and methanol. Thus, in methylamine one C—H bond located *trans* to the lone pair should be long and weak compared to the two C—H bonds orientated

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trans to the N—H bonds [3]. This pattern is reversed in methanol where two C—H bonds are weak and one C—H bond is strong [3].

Ab initio calculations reproduce satisfactorily the direction of the rotational axis of the methyl group in methylamine [6, 7, 8] and methanol [6, 7, 9]. In addition two different C—H bond lengths in the methyl groups of methylamine and methanol have been calculated [6, 10]. If the lone pair is located *trans* to a C—H bond a significant decrease of the C—H force constant is derived using an *ab initio* potential energy surface [6]. According to an analysis using localized orbitals the geometry of the methyl group arises from a combined interaction between the C—H bonds, the adjacent X—H bonds and the lone pair [10]. The preferred *trans* orientation of the C—F bonds and the lone pairs in CFH_2NH_2 and CFH_2OH has been explained by assuming a delocalization of the lone pair electrons into the antibonding C—F orbital [11]. Recently, the same type of orbital interaction has been used to explain the *ab initio* geometries of the methyl groups in methylamine and methanol [12]. Such a trans orientated electron donation has been first suggested by Hamlow et al. [13] to rationalise the *trans* lone pair effect. An orbital interaction scheme for the *trans* lone pair effect in CH_3NH_2 and CH_3OH has been derived by means of qualitative perturbation theory which failed to explain the different bond strengths in methylamine and methanol [14]. Thus, the *trans* lone pair effect is correctly reproduced by the SCF calculations. However, the difficulty remains to derive from correct SCF calculations an orbital interaction scheme which is based on perturbation theory. Therefore, the application of a perturbational method is desirable which retains the accuracy of the SCF calculation and produces an orbital interaction scheme. Such procedures have been proposed [15, 16, 17] and we apply the CNDO/2 SCF-perturbation theory [15] to derive an orbital interaction scheme for the *trans* lone pair effect in methylamine and methanol.

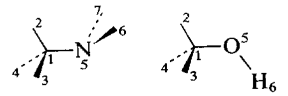
2. Results and Discussion

2.1. Methylamine

The CNDO/2 minimum geometry of methylamine has been determined using a Newton–Raphson procedure with numerical evaluation of the first and second order derivatives [18]. The geometrical parameters and their corresponding minimal values are recorded in Table 1. The CNDO/2 bond lengths and bond angles differ from the *ab initio* geometrical parameters which are close to the experimental geometry. Nevertheless, the CNDO/2 method indicates a slightly longer $C_1—H_2$ bond compared to the $C_1—H_3$ bond (see Table 1) in agreement with the conclusions of McKean [3]. Moreover, the tilt of the methyl group is reasonably reproduced.

Now, the isolated C—H frequencies [3] are used as a qualitative measure for different C—H bond strengths in the methyl group as concluded by McKean [3]. In the following we assume that these different bond strengths are reflected by the energies E^P arising when the C—H bonds are elongated by 0.1 Å. The E^P has

Table 1. Minimized CNDO/2 geometries of methylamine (X = N) and methanol (X = O) compared to *ab initio* calculations and experimental geometries. Bond distances are recorded in Å and angles in degrees. In the microwave studies [22, 23] the methyl groups are assumed as symmetric rotators. The tilt of the methyl groups is the angle between the C_3 axis and the C—X bond



	CNDO/2		*ab initio* [10]		exp.	
Param.	X = N	X = O	X = N	X = O	X = N [22]	X = O[23]
$C_1—H_2$	1.122	1.120	1.089	1.079	1.093	1.0936
$C_1—H_3$	1.121	1.121	1.081	1.085	1.093	1.0936
$C_1—X_5$	1.404	1.368	1.472	1.441	1.474	1.4246
$X_5—H_6$	1.071	1.033	1.005	0.967	1.011	0.9451
$<X_5C_1H_2$	114.1	108.5	113.7	106.0		
$<X_5C_1H_3$	110.4	111.8	108.6	111.9		
$<H_3C_1H_4$	107.4	108.1	107.7	109.1	109.28	108.38
$<C_1X_5H_6$	108.3	106.1	113.7	110.8	112.3	108.32
$<H_6X_5H_7$	104.3	—	110.6	—	105.52	—
tilt	2.5	2.2	3.4	3.9	3.5	3.16

been calculated directly using the SCF-perturbational approach [15]. The E^P values recorded in Table 2 are close to the E_{var} derived as the difference between the CNDO/2 energies for the distorted and the equilibrium geometries. Thus, the perturbational approach [15] retains the accuracy of the CNDO/2 calculation.

The E^P values designate the $C_1—H_2$ bond as weaker compared to the $C_1—H_3$ bond in agreement with the results of McKean [3]. In the following we attempt to determine the main effect which decreases the $C_1—H_2$ bond strength. Table 2 indicates that the smaller E^P for the $C_1—H_2$ bond distortion is primarely caused by a smaller E^1_{res} value. Since E^1_{res} is related to the capability of the equilibrium charge distribution to prevent a deformation of the equilibrium geometry [15], this capability seems to be less pronounced for the $C_1—H_2$ elongation than for a $C_1—H_3$ bond elongation (see Table 2). The total E^1_{res} can be resolved into energy increments E^1_{ii} for a localized orbital λ_i [19]. Therefore, we are in a position to determine which localized charge distribution $\lambda_i\lambda_i^\star$ decreases the $C_1—H_2$ bond strength predominantly. For this analysis Foster–Boys localized orbitals [20] are employed. Table 3 illustrates that the smaller E^1_{res} value for a $C_1—H_2$ distortion is due to the energy increment for the localized lone pair orbital. This result supports a charge distribution for the lone pair electrons facilitating a $C_1—H_2$ bond elongation more than a $C_1—H_3$ elongation.

In Fig. 1 energy increments E^1_{ii} [19] for the lone pair and the N—H localized orbital are recorded for different rotational angles α about the C—N bond. Between $\alpha = 0$ and $\alpha = 90$ degrees, the lone pair and the N—H bond have a similar weakening influence on the C—H bond strength (see Fig. 1). However, a *trans* orientated lone pair ($\alpha = 180°$) diminishes the $C_1—H_2$ bond strength more than a

Table 2. Perturbation energies E^P and the resolution into energy components [15] for an elongation of C_1-H_2 and C_1-H_3 bonds in methylamine and methanol. All values are recorded in kcal/mol. The Δ values are the difference between the *trans* lp and *trans* X—H contribution (X = N, O). For the numbering of the atoms see Table 1

		E_{var}	E^P	E^1_{res}	E^1_{ex}	E^1_{el}	E^1_{ND}	E^2_{res}	E^2_{ex}	E^2_{pol}	E^3
	C_1-H_2 *trans* lp	7.2627	7.2686	37.2607	7.4905	0.0231	−37.0917	−0.3882	−0.0183	0.0057	−0.0132
CH_3-NH_2	C_1-H_3 *trans* NH	7.3311	7.3407	37.5028	7.4939	0.0090	−37.2747	−0.3682	−0.0137	0.0033	−0.0117
	Δ	−0.0684	−0.0721	−0.2421	−0.0034	0.0141	0.1830	−0.0200	−0.0046	0.0024	−0.0015
	C_1-H_3 *trans* lp	7.3235	7.3322	37.3616	7.5328	0.0309	−37.2050	−0.3673	−0.0148	0.0061	−0.0121
CH_3-OH	C_1-H_2 *trans* O—H	7.3538	7.3568	37.5506	7.5200	0.0084	−37.3365	−0.3657	−0.0129	0.0045	−0.0116
	Δ	0.0303	−0.0246	−0.1890	0.0128	0.0225	0.1315	−0.0016	−0.0019	0.0016	−0.0005

Table 3. Energy increments E_{ii}^1 of E_{res}^1 [19] for the localized orbitals λ_i when the *trans* lp and *trans* X—H bonds (X = N, O) in methylamine and methanol are elongated by 0.1 Å. All values are recorded in kcal/mol.

○ characterizes the lone pair above the mirror plane, whereas ● designates the lone pair located behind the mirror plane. For the numbering of the atoms see Table 1

	λ_i	trans lp	λ_i	trans X—H	Δ
	C_1—H_2	38.9244	C_1—H_3	38.8791	0.0453
	C_1—H_3	−0.3439	C_1—H_2	−0.4142	0.0703
	C_1—H_4	−0.3439	C_1—H_4	−0.2943	−0.0496
CH_3—NH_2	C_1—N_5	−0.0627	C_1—N_5	−0.1690	0.1063
	N_5—H_6	−0.1814	N_5—H_6	−0.2033	0.0219
	N_5—H_7	−0.1814	N_5—H_7	−0.1355	−0.0459
	lp	−0.5505	1*p*	−0.1600	−0.3905
	C_1—H_3	38.9104	C_1—H_2	38.8791	0.0313
	C_1—H_2	−0.3766	C_1—H_3	−0.4092	0.0326
	C_1—H_4	−0.4638	C_1—H_4	−0.4092	−0.0546
CH_3—OH	C_1—O_5	0.0401	C_1—O_5	−0.1198	0.1599
	O_5—H_6	−0.2019	O_5—H_6	−0.0741	−0.1278
	lp○	−0.1537	1*p*	−0.1581	0.0044
	lp●	−0.3929	1*p*	−0.1581	−0.2348

trans located N—H bond corroborating the results of McKean [3]. This different behaviour accords also with the analysis performed by Flood et al. [10]: the $N_5C_1H_2$ angle is more influenced by a *trans* lone pair than by a *trans* orientated N—H bond [10].

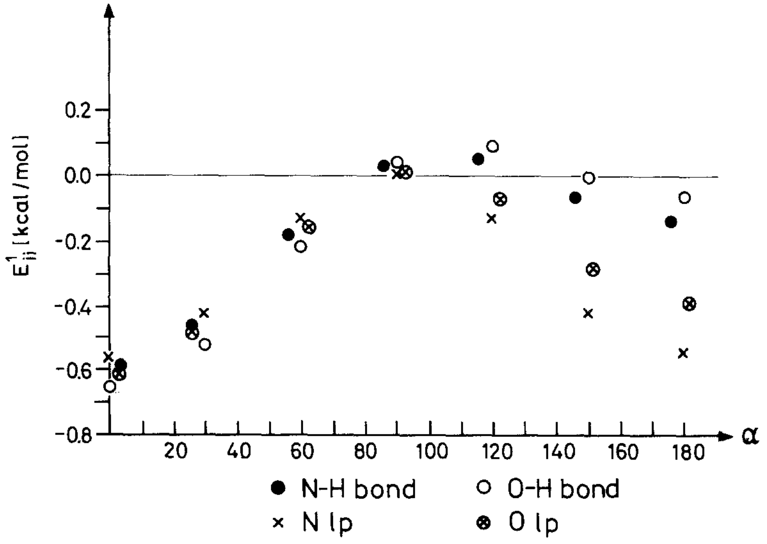


Fig. 1. Energy increments E_{ii}^1 [19] for the lone pair orbital and the X—H localized orbital when the C_1—H_2 bonds in methylamine and methanol are elongated. The E_{ii}^1 are recorded as a function of the rotational angle α about the C_1—X_5 bonds. All values are given in kcal/mol. For the numbering of the atoms see Table 1

In the following we investigate why a large negative E^1_{ii} for the localized lone pair orbital is calculated, when the C—H bond and the lone pair are *trans* orientated. For this analysis the form of the localized lone pair orbital is considered. In addition to the dominant lone pair contribution on the nitrogen, the orbital is significantly antibonding in the C_1—H_2 region; this finding is less pronounced in the C_1—H_3 region. Thus, the partitioning of E^1_{res} into E^1_{ii} for localized orbitals (see Table 3) and the form of the localized lone pair orbital indicate that the weakness of the C_1—H_2 bond is manifested in the C_1—H_2 antibonding character of the lone pair orbital. Now, we attempt to derive an orbital interaction scheme which explains the occurrence of the C_1—H_2 antibonding character. For this purpose an unperturbed problem is defined where the C_1—N_5 bond length R^0 is elongated by 0.1 Å. The C_1—N_5 bond distance is decreased to the equilibrium value R^0 and we calculate the energy contributions E^2_{ij} which arise from the interaction of the occupied localized orbital λ_i and the unoccupied localized orbital λ_j [19]. Using qualitative perturbation theory this extent of orbital interaction is estimated by considering the form of the orbitals and their energies [16]. The advantage of the SCF-perturbational approach is to provide energy quantities E^2_{ij} for orbital interaction which can be used to derive an orbital interaction scheme from a calculation [19]. The largest E^2_{ij} is due to the lone pair which interacts with the antibonding C_1—$N_5^\star$ and the antibonding C_1—$H_2^\star$ orbital (see Table 4). This latter *trans* orientated interaction introduces the antibonding character into the C_1—H_2 region of the lone pair orbital. Notice, the interaction of the lone pair orbital with the antibonding C_1—$H_3^\star$ orbital is much less than with the C_1—$H_2^\star$ orbital (see Table 4). Moreover, Table 4 illustrates that a *trans* orientated interaction occurs for all *trans* located orbitals but is more pronounced for the lone pair orbital.

2.2. *Methanol*

The minimized parameters of the CNDO/2 geometry are recorded in Table 1. As for methylamine bond lengths and bond angles are in poorer agreement with experiment than the *ab initio* geometry. Particularly, the C_1—O_5 bond length is too short which is a known CNDO/2 result [21]. Nevertheless, the asymmetry of

Table 4. Energy components E^2_{ij} of E^2_{res} [19] arising when the C_1—N_5 distance of methylamine is decreased from $R^0+0.1$ Å to R^0. The components E^2_{ij} result from the interaction of occupied and unoccupied localized orbitals of the unperturbed problem. All values are given in kcal/mol. For the numbering of the atoms see Table 1

	C_1—N_5	N_5—H_6	N_5—H_7	C_1—H_3	C_1—H_4	C_1—H_2	lp
N_5—$H_6^\star$	−0.0018	0.0000	−0.0006	−0.0100	$-\underline{0.1418}$	−0.0232	0.0000
N_5—$H_7^\star$	−0.0018	−0.0006	0.0000	$-\underline{0.1418}$	−0.0100	−0.0232	0.0000
C_1—$H_4^\star$	−0.0037	$-\underline{0.1782}$	−0.0332	−0.0006	−0.0062	−0.0018	−0.0464
C_1—$H_3^\star$	−0.0037	−0.0332	$-\underline{0.1782}$	−0.0062	−0.0006	−0.0018	−0.0464
C_1—$H_2^\star$	−0.0006	−0.0338	−0.0338	−0.0025	−0.0025	−0.0125	$-\underline{0.2674}$
C_1—$N_5^\star$	−0.0138	−0.3119	−0.3119	−0.1745	−0.1745	−0.1814	−0.3803

Table 5. Energy components E_{ij}^2 of E_{res}^2 [19] for the interaction of occupied and unoccupied localized orbitals of methanol. The E_{ij}^2 arise when the C—O distance is decreased from $R^0+0.1$ Å to R^0. All values are given in kcal/mol. For the numbering of the atoms see Table 1.

○ designates the lone pair above the mirror plane, whereas ● characterizes the lone pair behind the mirror plane

	C_1—O_5	O_5—H_6	C_1—H_2	C_1—H_3	C_1—H_4	lp○	lp●
C_1—H_3*	0.0000	−0.0395	−0.0018	−0.0138	−0.0037	−0.0521	−0.2667
C_1—H_4*	0.0000	−0.0395	−0.0018	−0.0037	−0.0138	−0.2667	−0.0521
C_1—H_2*	−0.0037	−0.1927	−0.0075	−0.0018	−0.0018	−0.0439	−0.0439
O_5—H_6*	−0.0006	−0.0006	−0.1368	−0.0094	−0.0094	0.0000	0.0000
C_1—O_5*	−0.0364	−0.3967	−0.1506	−0.1632	−0.1632	−0.4927	−0.4927

the methyl group and the difference in C—H bond lengths are reasonably reproduced. The C_1—H_3 bond is slightly longer than the C_1—H_2 bond (see Table 1). The corresponding perturbation energies E^P (see Table 2) designate the C_1—H_3 bond as weaker compared to the C_1—H_2 bond which accords with the conclusions of McKean [3]. Again, the main effect lowering the C_1—H_3 bond strength is indicated by a smaller E_{res}^1 value (see Table 2) arising from negative energy increments E_{ii}^1 for the *trans* lone pair and the O_5—H_6 localized orbital (see Table 3). Notice, the lone pair which is almost *cis* located to the C_1—H_3 bond diminishes the E_{res}^1 value less than the *trans* orientated lone pair. The energy increments E_{ii}^1 for the O_5—H_6 and the lone pair orbitals are recorded in Fig. 1 as a function of the rotational angle α about the C_1—O_5 bond. Qualitatively, the same angular dependence as for methylamine is derived. In a *trans* orientation to the C_1—H_2 bond the lone pair turns out to be more C_1—H_2 bond weakening than the O_5—H_6 bond. The large impact of the O_5—H_6 bond on the C_1—H_3 bond (see Table 3) is consistent with being almost *cis* orientated.

The lone pair orbital being *trans* located to the C_1—H_3 bond is characterized by an antibonding character in the C_1—H_3 bond region. This finding is supported by the orbital interaction scheme (see Table 5) evaluated in the same way as for methylamine. From all localized orbitals the two lone pairs and the O_5—H_6 orbitals interact preferentially with the antibonding C_1—O_5* and a *trans* located C—H* orbital (see Table 5). These orbital interactions introduce an antibonding character into the C_1—H_3 region of the *trans* lone pair and the O_5—H_6 orbital.

3. Summary and Conclusions

From the SCF-perturbational analysis the following rationalization for the *trans* lone pair effect on the C—H bonds in methylamine and methanol is derived. The electrons in the lone pair orbitals are partially delocalized into an antibonding C—H* orbital located *trans* to the lone pair. This effect causes an antibonding character in the *trans* C—H bond region of the lone pair orbital with a concomitant weakening of the C—H bond. The antibonding character seems to be an indicative criterion for the occurrence of the *trans* lone pair effect. We performed calculations on dimethylamine, trimethylamine and dimethylether to verify this result of the perturbational analysis. The antibonding character is present in all three molecules where a *trans* lone pair effect has been observed [3]. Thus, the perturbational analysis of CNDO/2 results supports Hamlow's explanation for the *trans* lone pair effect [13].

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