Rotational Isomerism and the Orientation of the Total Dipole Moment

Ivan Botskor
Abteilung Physikalische Chemie der Universität Ulm

Z. Naturforsch. **35a**, 748–756 (1980); received May 8, 1980

A method for determining the orientation of the total dipole moments of distinct rotamers of the same molecule is discussed. Utilizing solely the experimental dipole moments obtained with microwave spectroscopy (gas phase) and an approximate structure, the orientation of the dipole moment can often be determined without use of bond moment considerations. Experimental data from nine rotamer pairs are analyzed to illustrate the method.

Introduction

The Stark effect observed in microwave spectroscopy [1], [2] provides a highly accurate method for measuring the total dipole moment of molecules in the gas phase. But, due to the inherent μ^2 dependence of the Stark shifts, only the absolute values of the dipole moment components (in the principal axis system) can be obtained. The actual orientation of the dipole moment is, nevertheless, of importance as it is ultimately related to the electronic distribution and bonding characteristics of the molecule.

In most microwave work the choice between the possible orientations is generally based on bond moment considerations [3] (which implicitly also assumes polarities) or on additional information obtained by measurement of the dipole moment of isotopic species. In the latter case, the change of the mass distribution rotates the principal axis system and it is sometimes possible to determine the actual orientation ("isotope pulling effect", e.g. [4], [5]. If additional microwave Zeeman spectroscopy data are also available it is possible in some cases to determine the polarity and orientation of the total dipole moment [6], [7].

Results about a number of molecules which have two or more distinct rotameric forms have been published in the past [2], the main point of interest lying generally on the identification of the stable conformations and the potential barriers separating them. In many cases the dipole moments of the rotameric forms habe been also measured, and the present paper proposes a simple method utilizing these experimental values for establishing in some cases the relative orientation of the dipole moment for one or sometimes both conformations.

Model

The most general description of rotational isomerism is considering a molecule as being formed by two parts (arbitrarily named top and frame) bound by the internal rotation axis, see Figure 1a. The following considerations refer to those cases where: i) both top and frame are asymmetric tops, ii) the barriers hindering the internal rotation are sufficiently high so that each rotational isomer is observed (in the time scale used in microwave spectroscopy) as a distinct molecule.

The dipole moment of a molecule can be considered as the sum of more or less localized bond moments and charge distributions (e.g. lone electron pairs) in the molecule. The sum of these contributions for the frame and top separately are the corresponding group moments $\boldsymbol{\mu}_t$ (top) and $\boldsymbol{\mu}_f$ (frame). The vectorial addition of $\boldsymbol{\mu}_t$ and $\boldsymbol{\mu}_f$ is then the total dipole moment

$$\boldsymbol{\mu} = \boldsymbol{\mu}_{\text{top}} + \boldsymbol{\mu}_{\text{frame}} \tag{1}$$

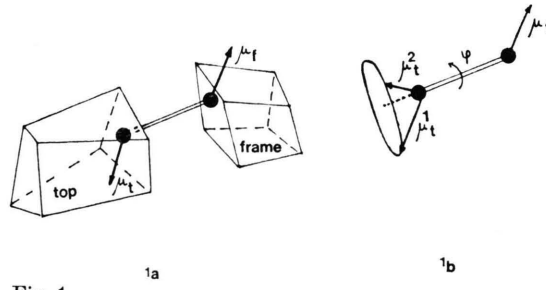


Fig. 1.

Reprint requests to Dr. Ivan Botskor, Abteilung Physikalische Chemie der Universität Ulm, Postfach 4066, D-7900 Ulm.

0340-4811 / 80 / 0700-0748 $ 01.00/0. — Please order a reprint rather than making your own copy.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung") beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

which in case of rotational isomerism can assume different values for each rotamer as the spacial relationship between $\boldsymbol{\mu}_t$ and $\boldsymbol{\mu}_f$ changes (Figure 1 b).

Two basic assumptions are made for the model: i) The structures of top and frame are considered rigid, thus structurally the rotamers only differ in the value of the dihedral angle Φ (see Figure 1 b). Non-bonded interactions, which often cause structural relaxations are not taken into account. ii) The group moments $\boldsymbol{\mu}_t$ and $\boldsymbol{\mu}_f$ are rigidly attached to the top and frame, respectively, and have the same magnitude independently of the rotameric form. The vectorial addition of $\boldsymbol{\mu}_t$ and $\boldsymbol{\mu}_f$ as a function of the dihedral angle can be easily visualized when the coordinate system chosen is such that one axis (X) coincides with the internal rotation axis. In this representation the components of the total dipole moment of the different rotamers can be written as a simple function of $\boldsymbol{\mu}_{top}$ and $\boldsymbol{\mu}_{frame}$

$$\left\|\begin{bmatrix}\mu_x{}^i\\ \mu_y{}^i\\ \mu_z{}^i\end{bmatrix}\right\| = \left\|\begin{bmatrix}1 & 0 & 0\\ 0 & \cos\Phi & \sin\Phi\\ 0 & -\sin\Phi & \cos\Phi\end{bmatrix}\begin{bmatrix}\mu_{tx}\\ \mu_{ty}\\ \mu_{tz}\end{bmatrix} + \begin{bmatrix}\mu_{fx}\\ \mu_{fy}\\ \mu_{fz}\end{bmatrix}\right\|, \tag{2}$$

where the angle Φ can have two or more different values for the distinct rotamers (e.g. $\Phi = 0$ *trans* or *cis*, $\Phi = 120°$ *gauche*). Although the total dipole moment is in principle[a] a function of the dihedral angle, or in other words, of the rotameric form, the component along the internal rotation axis, $\boldsymbol{\mu}_x{}^i$, remains invariant, as given in (2) and in Fig. (1 b), thus

$$|\mu_x{}^1| = |\mu_x{}^2|, \tag{3}$$

The actual usefulness of the rather trivial equation (3) can be seen when the considered XYZ coordinate system is related to the principal axis systems $A^iB^iC^i$ of the considered rotamers (e.g. i = *cis*, *gauche*). Given an approximate knowledge of the geometry the direction cosines d_{jk} between XYZ and $A^iB^iC^i$ can be calculated and the experimentally measured dipole moment components μ_a, μ_b, μ_c in the principal axis system related to the $\mu_j{}^i$ of (2):

$$|\mu_j{}^i| = \left|\sum_{k=a,b,c} d_{jk}\, s_k\, |\mu_k{}^i|\right|, \quad j = x, y, z. \tag{4}$$

The actual experimental information refers only to the absolute values of the components, namely $|\mu_a{}^i|$, $|\mu_b{}^i|$ and $|\mu_c{}^i|$. This sign indeterminacy is taken into account in (4) by giving the values $+1$ or -1 to the s_j terms and considering all distinguishable combinations (where for the orientation a change of all signs in row is not distinguishable):

Table 1

s_a	s_b	s_c
+1	+1	+1
+1	+1	−1
+1	−1	+1
+1	−1	−1

Using the experimental dipole moment and structural data for two distinct rotamers (e.g. *cis* and *gauche*) the values of $|\mu_x{}^1|$ and $|\mu_x{}^2|$ can be calculated with (4) and table (1) for all possible orientations. The required equality of $|\mu_x{}^1| = |\mu_x{}^2|$ for both rotamers allows a selection of the possible orientation of the dipole moment in one or both rotamers. The assumed rigidity, invariance of the group moments as well as structural errors and dipole moment measurement errors allow the aforementioned equality to hold only within a margin depending on the molecule considered. Nevertheless, even this approximate equality leads in many cases to an assignment of the orientation as it is shown in Figures 2 to 10.

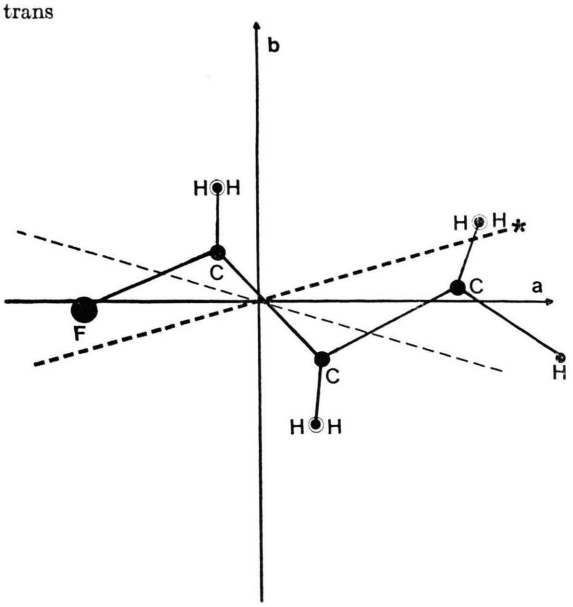
Examples

Ten rotameric pairs involving rotation around the C—C, C—N and C—O bonds are used as examples (Figs. 2—10) for the determination of the orientation of the total dipole moments. The structure utilized corresponds to the published values for *one* rotamer where the structure of the second rotamer was simply calculated by varying the dihedral angle. This assumed rigidity is most cases undoubtedly untrue and thus a source of error but necessary for a simple model. The dipole moment components utilized to calculate the possible projections of the total dipole moment $|\mu_x{}^i|$[a] on the internal rotation axis are the published values. The signs of the possible orientations coincide with those given in the principal axis systems in the figures[b] corresponding to each molecule. Those

[a] assuming that at least one of the group moments is different from zero and it is not parallel to the internal rotation axis.

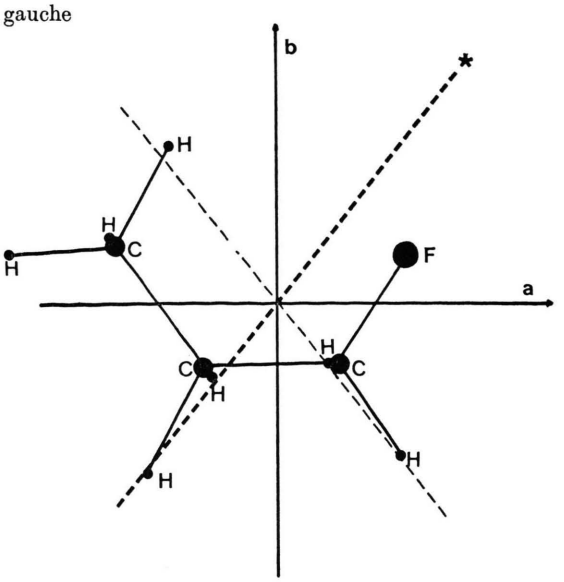
[a] in Debye. [b] Right hand system.

trans



a	*b*	$\lvert\mu_x\rvert^{\text{trans}}$
+	+	1.00 * bm
+	−	1.77

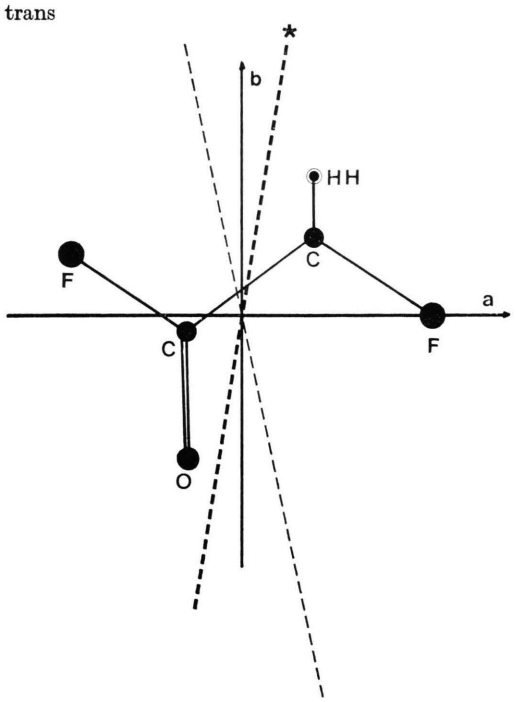
gauche



a	*b*	*c*	$\lvert\mu_x\rvert^{\text{gauche}}$
+	+	+	0.92 * bm
+	+	−	1.28
+	−	+	0.79
+	−	−	1.17

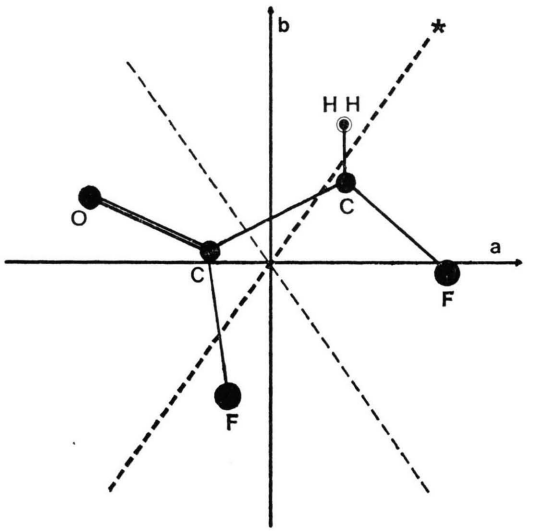
Fig. 2. propyl fluoride [8].

trans



a	*b*	$\lvert\mu_x\rvert^{\text{trans}}$
+	+	1.87 * bm
+	−	1.12

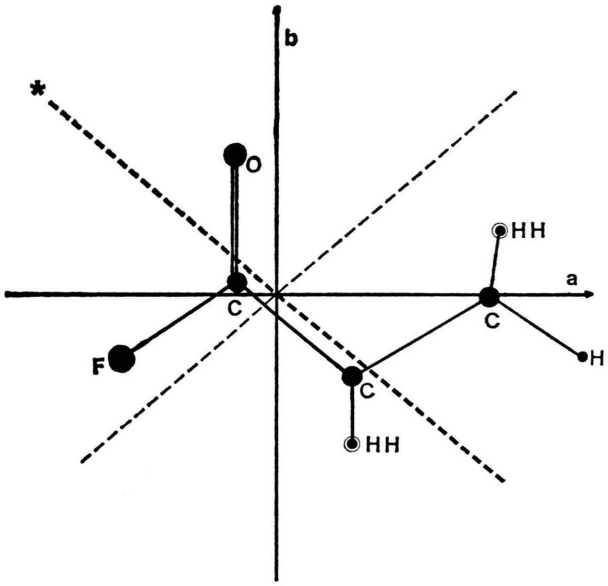
cis



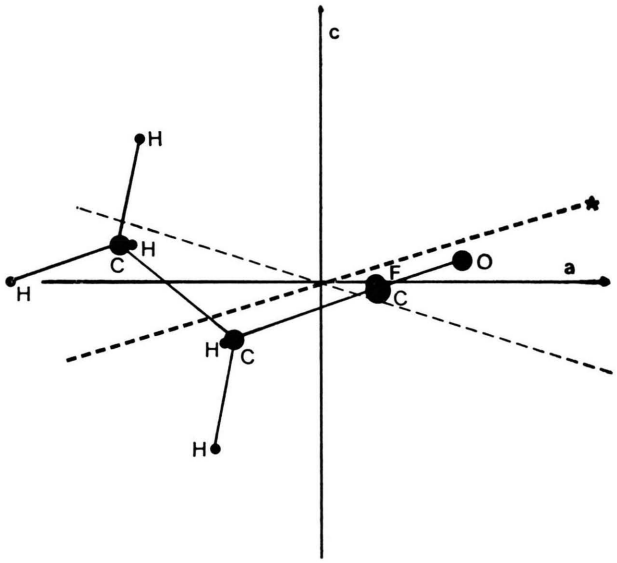
a	*b*	$\lvert\mu_x\rvert^{\text{cis}}$
+	+	1.83 * bm
+	−	0.24

Fig. 3. fluoroacetyl fluoride [9].

cis



gauche

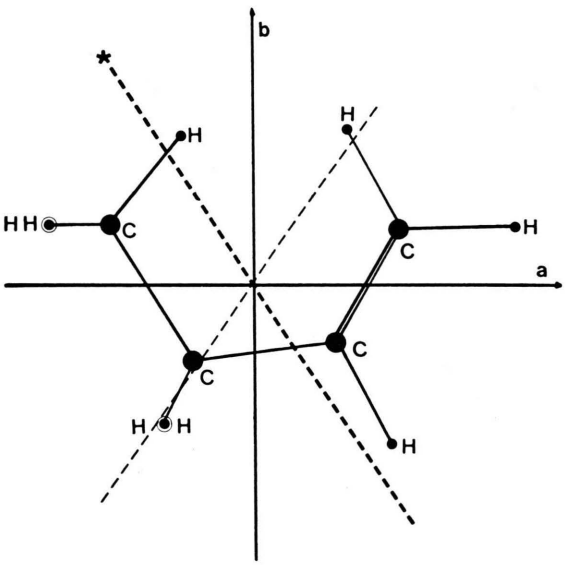


a	*b*	$\lvert\mu_x\rvert^{cis}$
+	+	0.66
+	−	2.89 * bm

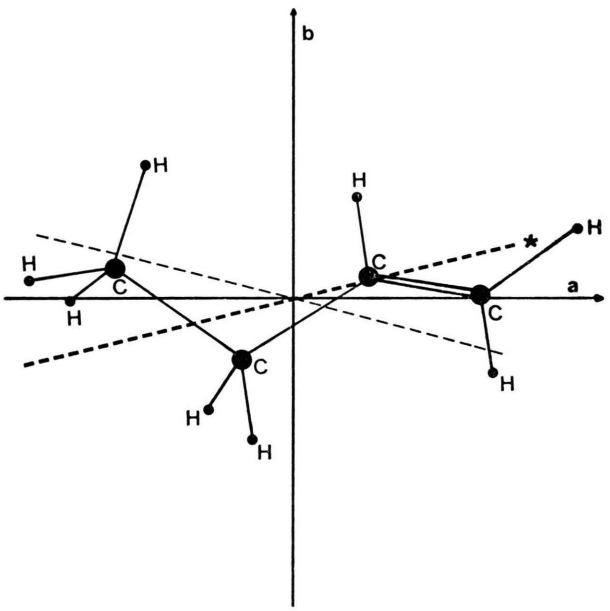
a	*b*	*c*	$\lvert\mu_x\rvert^{gauche}$
+	+	+	2.88 *
+	−	+	3.04 *
+	+	−	2.32
+	−	−	2.48

Fig. 4. propionyl fluoride [10].

cis



gauche

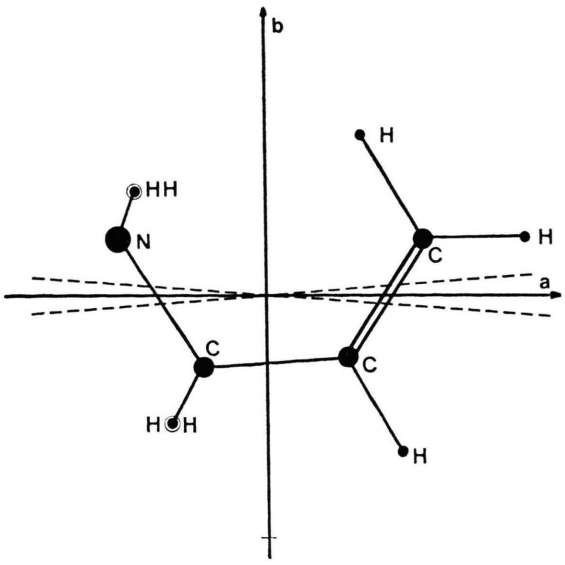


a	*b*	$\lvert\mu_x\rvert^{cis}$
+	+	0.39
+	−	0.34 *

a	*b*	*c*	$\lvert\mu_x\rvert^{gauche}$
+	+	+	0.34 *
+	+	−	0.32 * i
+	−	+	0.26
+	−	−	0.24

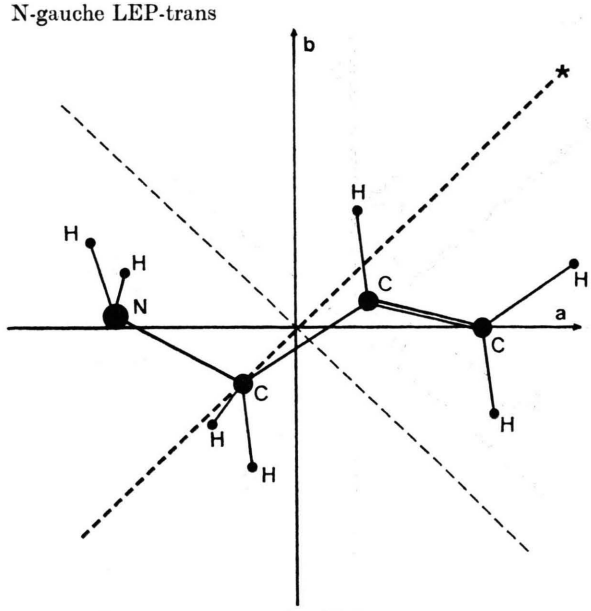
Fig. 5. Butene-1 [11].

N-cis LEP[a]-trans



a	b	$\lvert\mu_x\rvert^{N_C L_T}$
+	+	0.89 * bm, i
+	−	0.88 *

N-gauche LEP-trans

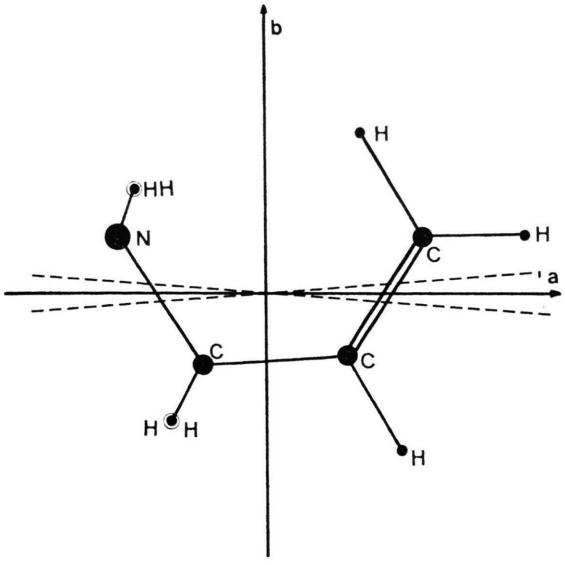


a	b	c	$\lvert\mu_x\rvert^{N_G L_T}$
+	+	+	1.04 *
+	+	−	1.00 *
+	−	+	0.32
+	−	−	0.27

[a] LEP = Lone Electron Pair.

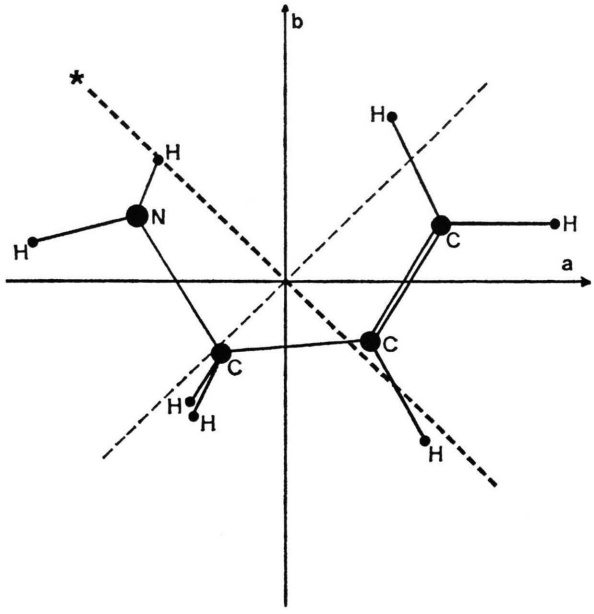
Fig. 6. Allylamine [12] [13]. Internal Rotation Axis CC.

N-cis LEP-trans



a	b	$\lvert\mu_x\rvert^{N_C L_T}$
+	+	0.43 * bm, i
+	−	0.48 *

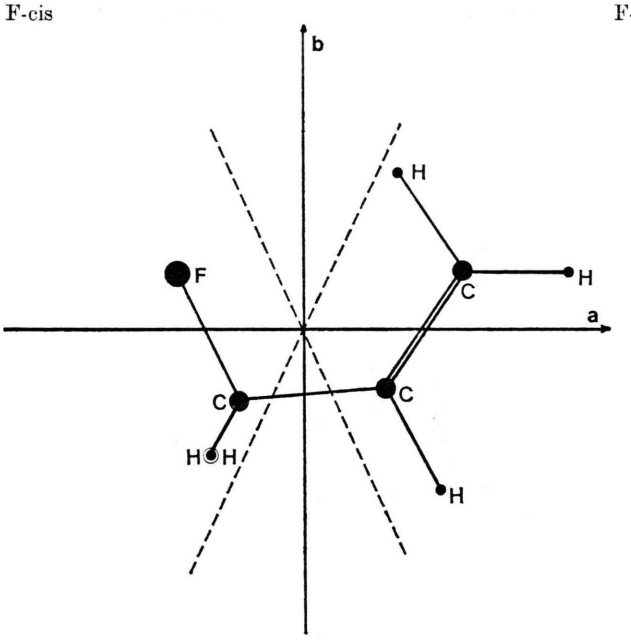
N-cis LEP-gauche



a	b	c	$\lvert\mu_x\rvert^{N_C L_T}$
+	+	+	0.25 *
+	+	−	0.20 *
+	−	+	1.05
+	−	−	1.11

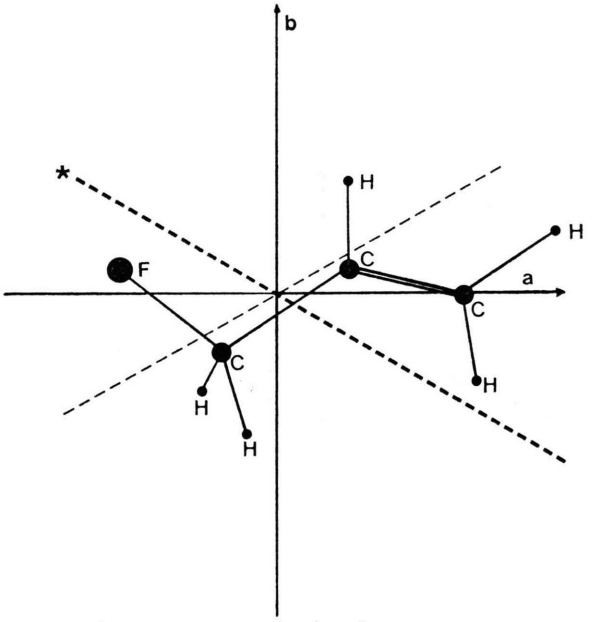
Fig. 7. Allylamine [5], [14]. Internal Rotation Axis CN.

F-cis



a	b	$\lvert\mu_x\rvert^{\text{cis}}$
+	+	0.85 *
+	−	0.62 * bm

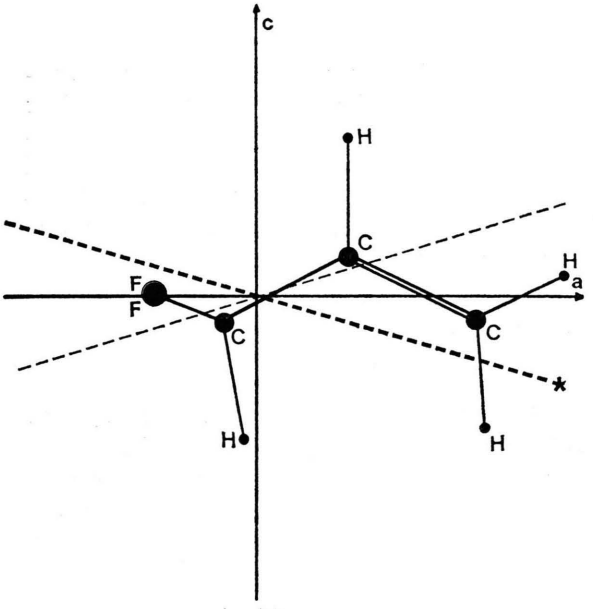
F-gauche



a	b	c	$\lvert\mu_x\rvert^{\text{gauche}}$
+	+	+	1.88
+	+	−	1.78
+	−	+	0.91 * bm, i
+	−	−	0.80 *

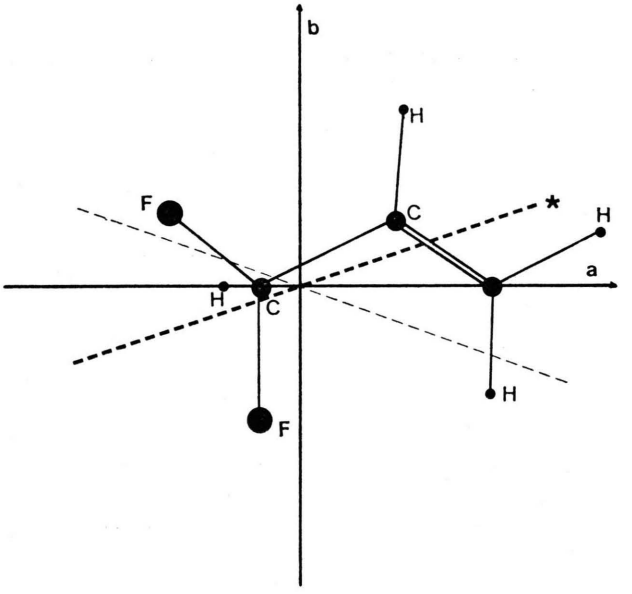
Fig. 8. 3-fluoropropene [15].

H-cis



a	c	$\lvert\mu_x\rvert^{\text{cis}}$
+	+	2.41
+	−	1.74 *

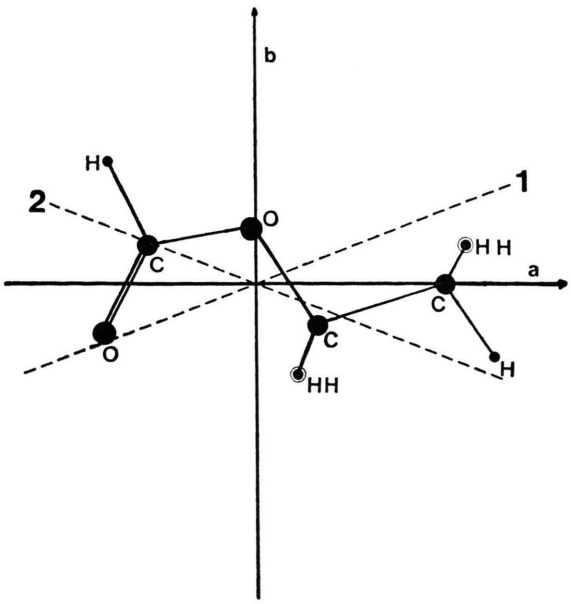
H-gauche



a	b	c	$\lvert\mu_x\rvert^{\text{gauche}}$
+	+	+	1.45
+	+	−	1.76 *
+	−	+	1.02
+	−	−	1.32

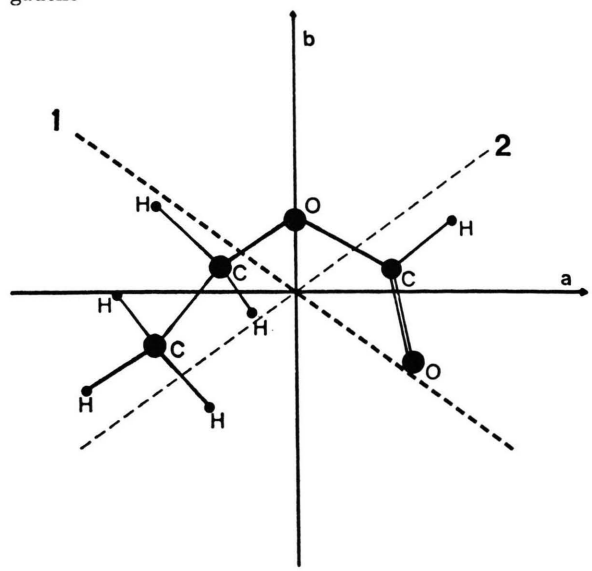
Fig. 9. 3-3′ difluoropropene [16].

trans



a	b	$\lvert\mu_x\rvert^{\text{trans}}$
+	+	0.49 (1)
+	−	1.62 (2)

gauche



a	b	c	$\lvert\mu_x\rvert^{\text{gauche}}$
+	+	+	1.66 } (2)
+	+	−	1.40 } (2)
+	−	+	0.69 } (1)
+	−	−	0.45 } (1)

Fig. 10 ethylformate [17].

orientations which are numerically consistent with the requirement $|\mu_x^1| \cong |\mu_x^2|$ are indicated by an asterisk * beside the numbers and the dashed lines in the figures. The obtained orientations can in some cases be compared to those which were determined by the authors by isotopic substitutions are indicated with i) and those considered reasonable through bond moment considerations with bm).

Two reservations should be made on the possible applicability of the condition $|\mu_x^1| \cong |\mu_x^2|$: i) When the internal rotation axis is parallel or very nearly parallel to a principal axis obviously there will be little or no variation in the value of the calculated $|\mu_x^i|$ components for the different orientations in that particular rotamer as in the example of allylamine N-*cis* lone-electron pair *trans* [Fig. (6, 7) and 3-fluoropropen *cis* (Fig. (9)], where the C—C internal rotation axis is almost parallel to the dipole moment. ii) A very nearly prolate or oblate molecule has to be dealt with special caution as the orientation of two principal axes is a very sensitive function of the structure. In these cases a relatively small structural error can easily rotate the principal axis system in the model with respect to their actual position (in which the dipole moment components were measured). Thus, the calculated direction cosines d_{jk} (Eq. (4)) will be quite different from the true values and the calculation will provide no useful results.

Perpendicular Dipole Moment Components to the Internal Rotation Axis

Under particular symmetry conditions $|\mu_y^i|$ and $|\mu_z^i|$ terms of (2) and (4) can also be of use in the determination of the orientation. Furthermore, their absolute value and *relative* polarity can be also determined. This calculation is only possible when one rotamer has C_s symmetry and the second one possesses no symmetry at all. In all examples considered, with the exception of fluoroacetyl fluoride, this condition is met.

By placing the Y axis of the XYZ coordinates system in the symmetry plane of the rotamer with

C_s symmetry, (2) can be written as

$$\left\|\begin{bmatrix}\mu_x^{\mathrm{i}}\\ \mu_y^{\mathrm{i}}\\ \mu_z^{\mathrm{i}}\end{bmatrix}\right\| = \left\|\begin{bmatrix}1 & 0 & 0\\ 0 & \cos\Phi & \sin\Phi\\ 0 & -\sin\Phi & \cos\Phi\end{bmatrix}\begin{bmatrix}\mu_{\mathrm{t}x}\\ \mu_{\mathrm{t}y}\\ 0\end{bmatrix} + \begin{bmatrix}\mu_{\mathrm{f}x}\\ \mu_{\mathrm{f}y}\\ 0\end{bmatrix}\right\|. \quad (5)$$

Consequently for the *trans* (or *cis*) rotamers $\Phi = 0$ and the following relation holds:

$$|\mu_y|^{\mathrm{trans}} = |\mu_{\mathrm{t}y} + \mu_{\mathrm{f}y}|, \quad (6)$$

whereas for the *gauche* form (Φ is the corresponding dihedral angle)

$$|\mu_y|^{\mathrm{gauche}} = |\cos\Phi\,\mu_{\mathrm{t}y} + \mu_{\mathrm{f}y}|, \quad (7)$$

$$|\mu_z|^{\mathrm{gauche}} = |-\sin\Phi\,\mu_{\mathrm{t}y}|. \quad (8)$$

The left hand terms of (7, 8) can be calculated using (4) and the actual group moment components $\mu_{\mathrm{f}y}$ and $\mu_{\mathrm{t}y}$ can then be expressed as

$$|\mu_{\mathrm{t}y}| = \left|\frac{|\mu_z|^{\mathrm{gauche}}}{\sin\Phi}\right|, \quad (9)$$

$$|\mu_{\mathrm{f}y}^{\pm}| = \left|\,|\mu_y|_{\pm}^{\mathrm{gauche}} \pm \operatorname{cotan}\Phi\,|\mu_z|^{\mathrm{gauche}}\right|. \quad (10)$$

The fact that the two group moment components $\mu_{\mathrm{t}y}$ and $\mu_{\mathrm{f}y}$ can have the same or opposite polarity has to be taken into account, thus duplicating the possible values which $\mu_{\mathrm{f}y}$ might have (Table 1). The addition

$$|\mu_y|_{\mathrm{pred}}^{\mathrm{trans}} = \left|\,|\mu_{\mathrm{t}y}| \pm |\mu_{\mathrm{f}y}^{\pm}|\right| \quad (11)$$

can then be compared to the equivalent term in the *trans* form (Eq. (6)).

For the true orientation they should be quite similar thus providing an additional criteria for assignment:

$$|\mu_y|_{\mathrm{pred}}^{\mathrm{trans}} \cong |\mu_y|^{\mathrm{trans}}. \quad (12)$$

The actual steps of the calculation are shown for propyl fluoride, Figure (2). The analysis utilizing the condition $|\mu_x|^{\mathrm{trans}} \cong |\mu_x|^{\mathrm{gauche}}$ identifies the true orientation in the *trans* form as being a) + b) + ($|\mu_x|^{\mathrm{trans}} = 1.00$ D) and in the *gauche* form as being most probably a) + b) + c) + ($|\mu_x|^{\mathrm{gauche}} = 0.92$ D) but so as to discard any other possibilities a calculation using the aforementioned steps is convenient and is presented in Table 2. It can be seen that of the eight possible values for $|\mu_y|_{\mathrm{pred}}^{\mathrm{trans}}$ only one (1.62 D) is sufficiently near to the $|\mu_y|^{\mathrm{trans}}$ value 1.72 D calculated with Eq. (4) for the known true orientation a) + b) + in the *trans* rotamer. The results confirm the assignment in the *gauche* form of a) + b) + c) + and allows the discarding any other possibility. In the course of the assignment the relative polarities of $|\mu_{y\mathrm{t}}|$ and $|\mu_{y\mathrm{f}}|$ as well as their absolute values have been also determined:

($|\mu_{y\mathrm{t}}|^{\mathrm{CH_2F}} \cong 1.71$ D,
$|\mu_{y\mathrm{f}}|^{\mathrm{ETHYL}} \cong 0.09$ D, with different polarities).

It should be stressed that the calculation makes in principle no a priori supposition whatsoever concerning the magnitudes, polarizations and directions of the considered group moments and only microwave data from one molecule is utilized. This allows for an independent determination which can be compared with results derived from other sources. As for example, if the $\boldsymbol{\mu}_{\mathrm{top}}$ is *assumed* in propyl fluoride to lie along the C—F bond, utilizing the *assigned* orientation for the total dipole moment and the *calculated* value of $|\mu_{y\mathrm{t}}|$, the bond moment is calculated as 1.83 D, a value which can be compared to bond moment values.

Ethyl formate is of particular interest as it serves as an example of the limitations and possibilities of this type of calculation, see Figure 10. No definite assignment can be made on the basis of the $|\mu_x|^{\mathrm{trans}}$ and $|\mu_x|^{\mathrm{gauche}}$ values, the only positive result is that two possible orientation pairs (I) *gauche* and

Tab. 2. Analysis of the assignment of the orientation of the dipole moment propyl Fluoride [8].

Orientation of the gauche form *a*	*b*	*c*	$\lvert\mu_y\rvert^{\mathrm{gauche}}$	$\lvert\mu_z\rvert^{\mathrm{gauche}}$	$\lvert\mu_{y\mathrm{t}}\rvert$	$\lvert\mu_{y\mathrm{f}}\rvert$ $=$ [a]	$\lvert\mu_{y\mathrm{f}}\rvert$ $\neq$ [b]	$\lvert\mu_y\rvert_{\mathrm{pred}}^{\mathrm{trans}}$ $=$ [a]	$\lvert\mu_y\rvert_{\mathrm{pred}}^{\mathrm{trans}}$ $\neq$ [b]
+	+	+	0.77	1.48	1.71	1.62	0.09	3.34	1.62 *
+	+	−	1.19	0.73	0.85	1.61	0.77	2.80	0.08
+	−	+	1.73	0.01	2.00	2.72	0.73	4.72	1.26
+	−	−	1.30	0.73	1.50	2.05	0.55	3.56	0.95

Assigned orientation	*a*	*b*	$\lvert\mu_y\rvert^{\mathrm{trans}}$
In the trans form	+	+	1.72 *

[a] Polarity of $\mu_{y\mathrm{f}}$ identical as $\mu_{y\mathrm{t}}$.
[b] Polarity of $\mu_{y\mathrm{f}}$ opposite as $\mu_{y\mathrm{t}}$.

trans or (II) *gauche* and *trans* can be distinguished (Table 3).

A second calculation involving the perpendicular component to the rotation axis, as was explicitely shown for propyl fluoride in Table 2, could also not lift the indetermination. Thus, in this case if no comparison with other molecules is made, the only positive conclusion is that the orientations are either (I) or (II) for both rotamers. That is if the orientation is assigned for one rotamer (e.g. isotopic substitution) the orientation in the other rotamer is also determined.

Table 3.

TRANS					GAUCHE				
	a	b	$\lvert\mu_x\rvert^{\text{trans}}$		a	b	c	$\lvert\mu_x\rvert^{\text{gauche}}$
(I)	+	+	0.49	↔	+	−	+	0.69
					+	−	−	0.45
or								
(II)	+	−	1.62	↔	+	+	+	1.66
					+	+	−	1.40

On the other hand orientation (I) would require $|\mu_y|^{\text{ethyl}} \cong 0.3\,\text{D}$ and $|\mu_y|^{\text{formate}} \cong 1.7\,\text{D}$ in contrast with orientation (II) $|\mu_y|^{\text{ethyl}} = 0.8\,\text{D}$ and $|\mu_y|^{\text{formate}} = 0.1\,\text{D}$. The results obtained with methyl formate [18] and other molecules with ethyl groups (e.g. in propyl fluoride, Table 2, $|\mu_y|^{\text{ethyl}}$ was calculated as 0.09 D) give strong grounds to the assumption that orientation (I) is most probably correct.

Acknowledgements

The present work was supported by the Deutsche Forschungsgemeinschaft. The support of Professor H. D. Rudolph is gratefully acknowledged.

[1] S. Golden and E. B. Wilson Jr., J. Chem. Phys. **16**, 669 (1948).
[2] W. Gordy and R. Cook, Microwave Molecular Spectra, Interscience Publishers 1970.
[3] C. P. Smyth, Dielectric Behaviour and Structure, McGraw Hill, New York 1955.
[4] P. Favero and J. G. Baker, Nuovo Cim. **17**, 734 (1960).
[5] E. Fischer and I. Botskor, Z. Naturforsch. **35a**, (1980) (in press).
[6] C. H. Townes, G. C. Dousmanis, R. L. White, and R. F. Schwarz, Discussions Faraday Soc. **19**, 56 (1955).
[7] W. Hüttner, Mei-Kuo Lo, and W. H. Flygare, J. Chem. Phys. **48**, 1206 (1968).
[8] Hirota, J. Chem. Phys. **37**, 283 (1962).
[9] E. Saegebarth and E. B. Wilson Jr., J. Chem. Phys. **46**, 3088 (1967).
[10] O. L. Stiefvater and E. B. Wilson, J. Chem Phys. **50**, 5385 (1969).
[11] S. Kondo, E. Hirota, and Y. Morino, J. Mol. Spectrosc. **28**, 471 (1968).
[12] G. Roussy, J. Demaison, I. Botskor, and H. D. Rudolph, J. Mol. Spectrosc. **38**, 535 (1971).
[13] I. Botskor, H. D. Rudolph, and G. Roussy, J. Mol. Spectrosc. **52**, 457 (1974).
[14] I. Botskor and H. D. Rudolph, J. Mol. Spectrosc. **71**, 430 (1978); I. Botskor, J. Mol. Spectrosc. **75**, 10 (1979).
[15] E. Hirota, J. Chem. Phys. **42**, 2071 (1965).
[16] I. Botskor and E. Hirota, J. Mol. Spectrosc. **61**, 79 (1976).
[17] J. M. Riveros and E. B. Wilson Jr., J. Chem. Phys. **46**, 4605 (1967).
[18] R. F. Curl Jr., J. Chem. Phys. **30**, 1529 (1959).