Amplitudes Carrées Moyennes de Vibration

A partir des champs de force précédents, nous avons calculé les racines carrées des amplitudes quadratiques moyennes de vibration de CH_3NO_2, CH_3NHNO_2, $(CH_3)_2NNO$ et $(CH_3)_2NNO_2$[18,19]. Ces amplitudes sont tout à fait comparables pour des groupements identiques, ce qui met en évidence l'auto-cohérence de nos champs de force (tableau XVII).

Rademacher et Stølevik ont déterminé par diffraction électronique les paramètres structuraux et les amplitudes carrées moyennes de vibration de la diméthylnitramine et de la diméthylnitrosamine[10].

Les racines carrées sont proches des valeurs que nous avons trouvées (tableau XVII). Les plus grandes différences sont observées pour u(C - - - - C) où u(N_2 - - - - H) dans ce dernier cas, l'écart peut être dû à l'anharmonicité des liaisons CH.

Nos résultats sont également comparables à ceux publiés dans la littérature pour les molécules comportant des groupements identiques. Ainsi, les valeurs obtenues par Cyvin pour les racines carrées des amplitudes quadratiques moyennes de la molécule NO_2 à 298°K[20] et celles des liaisons CH de nombreuses molécules[21] sont presque identiques aux nôtres. De même, les amplitudes de CH_3NH_2 et $(CH_3)_2NH$ publiées par Dellepiane *et al.*[22] sont voisines de celles de CH_3NHNO_2.

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Assignments of Electronic Transitions in Methanal Azine and Related Molecules

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Résumé: *La méthode des orbitales moléculaires π de Pople a été appliquée aux rotamères cisoïdes et transoïdes du 1,3-butadiène, méthanal azine, éthanedial et du propénal. L'absorption électronique vers 40000 cm⁻¹ pour le 1,3-butadiène est attribuée à un second conformère, et celle à 44000 cm⁻¹ pour le méthanal azine, au second rotamère gauche. D'autres propriétés des rotamères cisoïdes sont prévues. On reporte d'autres résultats sur le spectre électronique du radical libre méthylèniminyle.*

Abstract: *Pople π-molecular-orbital theory has been applied to cisoid and transoid rotamers of butadiene-1,3, methanal azine, ethandial and propenal. Electronic absorption in the region of 40,000 cm⁻¹ for butadiene-1,3, is assigned to a second conformer, and absorption about 44,000 cm⁻¹ for methanal azine is assigned to the second, gauche rotamer. Other properties of cisoid rotamers are predicted. Further measurements of the electronic spectrum of the methyleniminyl free radical are reported.*

Introduction

Electronic absorption spectra of methanal azine ($H_2C=N-N=CH_2$) and the methyleniminyl free radical ($H_2C=N\cdot$) have already been described[1]. For the radical, further information on the nature of the electronic transition was sought from spectra under high resolution, and is discussed here. Of the three absorption regions of the azine in the accessible ultraviolet region, qualitative assignments were readily proposed for two transitions. Another suggestion transition was based on results of molecular orbital computations[2] for ethene (C_2H_4) which at that time appeared to indicate the existence of a C-H antibonding orbital, with partial Rydberg character, which lay at less energy than the π^*-orbital. Later computations[3] showed however that the small energy of this σ^*-orbital was largely an artefact arising from the nature of the virtual orbital computations in a limited basis set. Thus the foundation for an assignment of the second azine absorption region had largely evaporated. Following direct detection of rotational isomers of both propenal ($H_2C=CH-CH=O$)[4] and ethandial ($O=CH-CH=O$)[5] from their electronic absorption spectra in the visible region, a second conformer of methanal azine has also been deduced to exist in electron diffraction experiments[6]. A second conformer of butadiene-1,3 ($H_2C=CH-CH=CH_2$) has also been indirectly detected by means of the temperature dependence of proton magnetic resonance signals[7].

To investigate the properties of these diene-type molecules by wave-mechanical computations seems timely, but the best approach for this objective is uncertain. Complete *ab initio* computations of sufficient accuracy for these relatively large molecules are still impracticable. Where *ab initio* computations were attempted[8] on butadiene-1,3, these were not complete, as the geometrical structure of only the more stable conformer was assumed, and the calculated transition wavenumbers were in poor agreement with experimental values. Thus semi-empirical methods seem required. Of those available, the Pople π-electron method[9] continues to prove extremely useful[10] in electronic spectral assignments, although only transitions within the π valence orbitals can be treated. Despite the fact that fine structural details relevant to interesting questions of isomerism are not encompassed by this method, it has been employed in this study. No method available at this time can, it is believed, provide an accurate account of all features of structure and excitations of these large molecules having only low symmetry.

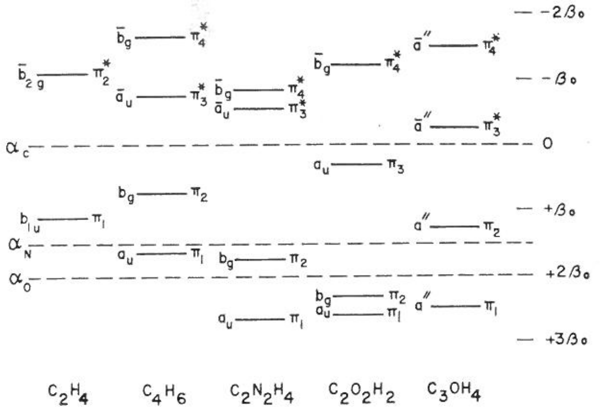


Figure 1. Relative orbital energies of diene-type molecules from Hückel calculations.

Method

Based on zero-differential-overlap π-electron molecular-orbital theory[9], the computational method[11] first forms the Hückel matrix[12] to derive relative eigenvalues and zero-order wavefunctions. Parameters for these are the Coulomb integral, $\alpha_x = \alpha_c + h_x\beta_o$, and the bond integral, $\beta_{xy} = k_{yx}\,\beta_o$, for the atoms in the π-system, where β_o is the basic resonance integral; values of k_{xy} and h_x, embodying corrections[12] for non-aromatic bonds and for atoms other than carbon in the conjugated chain, are listed in Table I with the relative eigen-

Table I. — Huckel parameters [12] for some diene-type molecules and the resulting eigenvalues

	$h_c = 0$ $h_N = 1.5$ $h_o = 2.0$	$k_{c=c} = 1.1$ $k_{c-c} = 0.9$ $h_{N-N} = 0.6$	$k_{5=N} = 1.2$ $k_{c=o} = 1.0$	
	$H_2C=C-C=CH_2$	$H_2C=N-N=CH_2$	$O=CH-CH=O$	$H_2C=CH-CH=O$
$(E_1 - \alpha_c)/\beta_o$	1.6385	2.6445	2.5913	2.4818
$(E_2 - \alpha_c)/\beta_o$	0.7385	1.7316	2.3114	1.2650
$(E_3 - \alpha_c)/\beta_o$	−0.7385	−0.5445	0.3087	−0.2591
$(E_4 - \alpha_c)/\beta_o$	−1.6385	−0.8316	−1.2114	−1.4877

Table II. — Calculated and observed structure, orbital energies and ionisation energies, relative energies, and dipole moments of transoid and cisoid rotamers of diene-type molecules, A = B – C = D.*

	$H_2C=CH-CH=CH_2$		$H_2C=N-N=CH_2$		$O=CH-CH=O$		$H_2C=CH-CH=O$	
	Trans.	Cis.	Trans.	Cis.	Trans.	Cis.	Trans.	Cis.
Calculated								
R_{AB}, pm	134.7	134.7	127.8	127.6	124.6	124.6	134.9	135.0
R_{BC}, pm	145.7	145.7	141.1	141.8	146.6	146.4	145.1	145.0
R_{CD}, pm	134.7	134.7	127.8	127.6	124.6	124.6	125.2	125.3
μ_e, C m × 10^{30}	0	0.51	0	6.29	0	10.5	10.7	9.4
$\Delta E_{(CIS-TRANS)}$, cm^{-1}	164		1060		350		6	
$-OE_1$, eV	9.6	9.6	10.7	10.7	12.9	12.8	11.0	11.0
$-OE_2$, eV	12.9	12.9	14.0	14.2	15.0	14.9	14.0	13.9
Observed								
R_{AB}, pm	134.5[a]	—	127.8[b]	(127.8)[b]	121.2[c]	(121.2)	134.5[e]	—
R_{BC}, pm	146.5	—	141.8	(141.8)	152.6	150.5[d]	148.4	—
R_{CD}, pm	134.5	—	127.8	(127.8)	121.2	(121.2)	121.2	—
$<ABC$, °	123.3	(127)	111.4	(111.4)	121.2	123.9	120.3	(124)
$<BCD$, °	123.3	(127)	111.4	(111.4)	121.2	123.9	123.27	(127)
μ_e, C m × 10^{30}	0	—	0	—	0	16.0	10.03	—
$\Delta E_{(CIS-TRANS)}$, cm^{-1}	735[f]		410[b]		1125[g]		700[h]	
IE_1, eV	9.0[i]	—	—	—	10.6[j]	—	10.1[k]	—
IE_2, eV	11.34	—	—	—	12.2	—	10.9	—

*Values in parentheses are assumed; dashes indicate unmeasured values.

[a] Reference 19.
[b] Reference 6.
[c] Reference 19.
[d] Reference 30.
[e] Reference 6.
[f] Reference 7.
[g] Reference 5.
[h] Reference 4.
[i] Reference 16.
[j] Reference 17.
[k] Reference 18.

values for the molecules treated. The relative orbital energies, illustrated in the figure, reflect the influences of increased nuclear charges relative to carbon. Although the Hückel treatment ignores conformation, relative orbital energies from further treatment are insensitive to effects of cisoid — transoid isomerism, so that the figure usefully depicts the pertinent effects without the complications of isomerism.

These zero-order wavefunctions are then employed in an iterative self-consistent field treatment in which bondlengths were also varied to minimise the total energy. In this semi-empirical treatment, one-centre electron-repulsion integrals were approximated by the difference of valence-state ionisation energy and electron affinity; two-centre repulsion integrals were determined by the relation of Mataga and Nishimoto[13]. The scaling factor K in the Wolfsberg-Helmholz approximation[14] for the two-centre resonance integral was separately fitted for singlet and triplet states of benzene. With K = 0.464 for singlet states and 0.555 for triplet states, the first three excited singlet states and two triplet states of benzene were generated in good agreement with experimental values. The computed conformational effects arose from the inclusion in the SCF treatment of resonance integrals between all atomic orbitals in the π-system, whether or not on neighbouring atoms. All bond lengths within the π-system were optimised (for the ground state) during the SCF iterations; interbond angles were fixed at known values where possible, otherwise estimated to take account of non-bonded repulsions of atoms in the σ-framework. The computations thus performed were for two conformers of each molecule, assumed planar, and differing essentially only in orientation of moieties about the central 'single' bond so as to generate s-cisoid and s-transoid rotational isomers. Some numerical results are summarised in Table II.

For relative energies of excited electronic states, the geometrical structure of the ground state was retained. Configuration interaction, including four singly excited configurations for each rotamer, was employed to take account of electron repulsion in order to obtain realistic estimates of transition wavenumbers. The results are presented in Table III. As the excited states were presumed to have ground-state geometrical structures, comparisons with observed maxima, not with electronic origins, in absorption spectra are appropriate. The physical significance of the wavenumbers and oscillator strengths are ±500 cm^{-1} and ±25 per cent respectively, depending upon the approximate wavefunctions. Wavenumbers and oscillator strengths predicted for third and fourth singlet and triplet transitions have not been included in Table III; because mixing of these $\pi^*\leftarrow\pi$ states with $\sigma^*\leftarrow\sigma$ states of comparable energy undoubtedly occurs, such calculated values are unlikely to be quantitatively meaningful.

Table III — Wavenumbers (cm^{-1}) predicted for transitions from the ground state of cisoid and transoid rotamers of diene-type molecules to their excited singlet and triplet states, with oscillator strengths for singlet-singlet transitions.*

	$H_2C=CH-CH=CH_2$		$H_2C=N-N=CH_2$		$O=CH-CH=O$		$H_2C=CH-CH=O$	
	Trans.	Cis.	Trans.	Cis.	Trans.	Cis.	Trans.	Cis.
$\triangle E_1^S$	48520	46390	50480	44170	56460	54740	49870	48120
f_1	1.07	0.58	0.69	0.155	0.91	0.48	0.90	0.55
$\triangle E_2^S$	56550	56510	55530	54880	64580	63730	62640	61990
f_2	0	0.056	0	0.12	0	0.021	0.146	0.041
$\triangle E_1^T$	21070	20560	25000	21920	20920	20440	21630	21400
$\triangle E_2^T$	35540	35660	31840	31150	35160	34930	37160	37380

*Experimental values are given in the main text.

Discussion

Four molecules, all of the diene type, were treated theoretically in this work: butadiene-1,3, methanal azine, ethandial and propenal. Whilst interest was primarily directed to the first two substances, the carbonyl compounds were included because their rotational isomers are better established. After some general comments, each molecule will be individually discussed.

The values in Table II show that the relative energies of the rotamers were poorly calculated; as the computations take no direct account of the σ-electron system, including hydrogen atoms or lone pairs on N or O atoms, this result is expected. The magnitudes of calculated orbital energies are always larger than the ionisation energies[15] measured in photo-electron experiments for butadiene-1,3[16], ethandial[17] and propenal[18]. The differences, ranging from 0.5 - 3.1 eV (4,000-25,000 cm^{-1}), are smaller for butadiene than for the carbonyl compounds. As the geometrical structure and other properties of both s-transoid butadiene and methanal azine are generally well reproduced by the computations, the ionisation energies of π-orbitals of the azine may be predicted to be ~10 and ~12.5 eV. In any case the very small differences between computed orbital energies for cisoid and transoid rotamers of all four compounds suggest that photoelectron spectroscopy will prove ineffective in detecting the less abundant rotamers by means of ionisation of π-electrons.

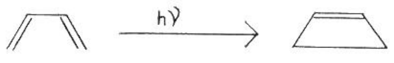
Butadiene-1,3

Except as noted above, ground-state properties of the transoid rotamer are well reproduced. Corresponding bondlengths[19] between adjacent carbon atoms within each rotamer are predicted to be identical; predicted bondlengths of the cisoid rotamer were insensitive to small changes of interbond angles. The dipole moment predicted for the cisoid rotamer is about half that of propene[20], consistent, in association with the small abundance, with the difficulty of detecting this rotamer by microwave spectroscopy[21]. The second rotamer in solution was however deduced[7] to be nonplanar; but with the estimated dihedral or torsional angle of 20°, and with the known large amplitudes of torsional vibrations, this conformer must be regarded as quasi-planar[22].

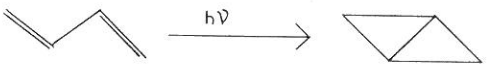
The first singlet-singlet transition of the transoid rotamer agrees well with the experimental absorption maximum, 47,700 cm^{-1}, but the computed oscillator strength is too large by half[1]. The calculated wavenumbers for the triplet state transitions agree well with the experimental adiabatic wavenumbers, 20,800 and 34,700 cm^{-1} [23]. The large differences between these quantities and those corresponding to vertical transitions[23], 26,000 and 39,500 cm^{-1}, indicate substantial changes of equilibrium geometry between the ground state and these triplet states.

In common with past theoretical investigations[24,25], the first singlet-singlet transition of the cisoid rotamer is predicted to have a smaller transition wavenumber than that of the transoid rotamer, in this case by 2000 cm^{-1}. Our spectra[1], similar to the standard spectrum[26], show a gradual onset of absorption extending, at great optical thickness, to 39,000 cm^{-1}, much more gradual than is consistent with an exponential decrease of population of vibrationally excited molecules in the ground state of the transoid rotamer. But there is no trace of even the most diffuse structure between 39,000 cm^{-1}, and 46,000 cm^{1-} near the apparent origin of the dominating transition[1]. If one assumes a similar pattern of vibrational levels for both rotamers in the ground state, and using the ratio of predicted oscillator strengths as a measure of relative absorbance of the rotamers, whether planar or not, one can estimate that the gradual onset of absorption near 40,000 cm^{-1} would be consistent with the presence of a second rotamer, absorbing in this region, to the extent of 1.2 ± 0.3 per cent at 308K. Such a relative abundance is associated with an energy difference equivalent to 950 ± 50 cm^{-1}, to be compared with 735 ± 15 cm^{-1} from the magnetic resonance experiments[7]; the agreement is satisfactory in view of the assumptions. The very diffuseness of the absorption makes a definite assignment almost impossible.

There is however definite chemical evidence for the existence of a second rotamer, cisoid or gauche, because, for electrocyclic or some Diels-Alder reactions, such a conformation is required to be adopted before (or possibly during) the reactive process. Photochemical evidence is even more convincing. The major product[26] of irradiation at 39,413 cm^{-1} of butadiene-1,3 in dilute solution is cyclobutene, obviously favoured to be formed from a cisoid rotamer:



whereas the minor product bicyclo[1.1.0] butane seems favoured to be formed from the far more abundant transoid rotamer:



Thus the attribution of absorption in the 39,000-45,000 cm^{-1} region to a second conformer of butadiene-1,3, cisoid or slightly skewed, is compatible with both theoretical and experimental observations. The large difference between calculated absorption maximum, at 46,400 cm^{-1}, and the apparent onset of absorption near 39,000 cm^{-1} would seem to indicate a large geometry change between the two combining states, analogous to the singlet-triplet transitions of the transoid rotamer. Efficient photochemical isomerisation could contribute to the diffuseness of the absorption.

The features in the 5.0 - 5.5 eV region of the electron impact spectra[23] are better attributed to this allowed transition of the less abundant rotamer than to other effects.

Methanal azine

The predicted bondlengths for the transoid rotamer are in good agreement with those deduced both from vibration-rotational spectra[27] and from electron diffraction[6], although the parameters in the bond order — bondlength relations[11] used in the computations were not based on these acyclic azines. The first predicted singlet-singlet electronic transition can easily be associated with the intense absorption[1] at 50,400 cm^{-1} (origin) or 51,700 cm^{-1} (maximum), consistent with the earlier $\pi^* \leftarrow \pi$ assignment[1]. As previously for benzene and butadiene, the oscillator strength of this transition seems to be considerably overestimated.

A second rotamer of methanal azine in electron diffraction experiments[6] was deduced to have a non-planar ground state. Predictions here for a planar cisoid conformer include a moderate dipole moment, relevant to microwave absorption lines reported earlier[29], and a N-N bondlength slightly but significantly greater than for the transoid rotamer. Except for the torsional angle, corresponding bondlengths of both rotamers were assumed equal in the diffraction analysis[6]. Although the π-orbital energies for each conformer are predicted to be similar, a large difference in first singlet-singlet π-excitation wavenumbers is indicated. In fact, a distinct progression of bands appears in the methanal azine absorption spectrum at the predicted position, the absorption maximum being ~44,150 cm^{-1} [1]. A long progression in a vibration of wavenumber appropriate to a skeletal bending or torsional mode rises from an apparent origin near 40,000 cm^{-1}, above the continuum attributed to a $\pi^* \leftarrow \pi$ transition[1]. Occupancy of the π_3^*-orbital could favour planarity, so the form of the contour, having only one observable maximum, would be consistent with a transition from a non-planar ground state to a planar excited state. (With the known large amplitude of torsional vibration in the ground state[6], a non-planar excited state would be expected to be indicated by a double maximum in the absorption profile). The ratio of computed oscillator strengths combined with the observed integrated intensities yields a relative abundance of a second rotamer consistent with the deducted energy difference[6]. Thus the assignment of the 44,000 cm^{-1} absorption of methanal azine to a $\pi^* \leftarrow \pi$ transition of a second rotamer solves an outstanding problem, and with the support of all experimental and theoretical data is confidently proposed.

Ethandial and Propenal

Prediction of properties of ethandial from computations within the π-electron approximation seems doomed to failure, because the experimental bondlength exceeds the value in the bond order — bondlength relation[11] for zero π-bond order. The inescapable inference is thus that there is little or no conjugation of the carbonyl moieties. As the computations greatly overestimate the extent of the interaction, any results of these computations must be suspect. However it is notable that a slight decrease of central bondlength is here predicted, and observed[30], from transoid to cisoid rotamers, in contrast to the predicted increase for methanal azine. Also the less stable rotamer is planar in both electronic states[5].

Likewise for propenal, structural predictions are not good, presumably for similar reasons. Electronic spectra of propenal in the visible and near ultraviolet regions (<30,000 cm^{-1}) have indicated the presence of a second rotamer[4], apparently planar in both ground and excited states. Unlike ethandial, no microwave absorption of a second rotamer has yet been reported[31]. An intense absorption continuum with maximum near 52,000 cm^{-1} [32], necessarily attributed to the abundant transoid rotamer, probably masks any adjacent diffuse absorption by a much less abundant second rotamer.

Methyleniminyl free radical

This radical, most conveniently produced by photodissociation of its dimer methanal azine[33], was one of the first polyatomic free radicals for which an experimental oscillator strength was obtained[1]. The well-formed profiles of a few bands observed under low resolution suggested that discrete rotational fine structure might be observable under high resolution. Analysis of such structure would, it was hoped, yield information on the nature of the electronic transitions as well as structural parameters. Measurements, on a 10.7 metre Eagle spectograph, with 0.3 cm^{-1} spectral slit width in the fourth order of a 600 groove-per-millimetre grating at the National Research Council laboratories in Ottawa, failed however to show any discrete fine structure for either H_2CN or D_2CN. However band centres were measured with increased accuracy, and a further weak band was identified. Results are given in Table IV. Vibrational analysis is not particularly aided by the new information. The best interpretation of the spectra is that the two prominent bands of each isotopic molecule represent different electronic transitions both originating in the ground vibronic state: a similar situation may apply to the F_2CN radical[34]. Experimental proof of the true diffuseness of the vibronic bands means that we can have confidence in the previously derived values of the maximum absorption coefficients[35] and f-value[1]. The former are 310 ± 150 1 mol^{-1} cm^{-1} at 35075 cm^{-1} and 600 ± 300 1 mol^{-1} cm^{-1} at 35,620 cm^{-1}, both for H_2CN. Roughly half the total f-value, $(4 \pm 2) \times 10^{-4}$, applies to each of these bands.

Table IV. — Band centres (cm^{-1}) in the electronic absorption spectrum of the methyleniminyl free radical obtained in vapour-phase flash photolysis.*

H_2CN		HDCN		D_2CN	
ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
35075	0	(35045)	0	35036	0
35620	545	(35550)	505	35481	445
		(36310)	1265	35696	660
				(36115)	1079
				(36930)	1894

*Values in parentheses are previous measurements[1].

Conclusion

Computations by the Pople π-electron method have indicated that cisoid rotamers of diene-type molecules can be detected more easily by valence shell ($\pi^* \leftarrow \pi$) electronic transitions than by photoelectron spectra of π excitations. Absorption in the 40,000 cm^{-1} region for butadiene-1,3 and near 44,000 cm^{-1} for methanal azine is attributed to $\pi^* \leftarrow \pi$ transitions of conformers in small abundance relative to the predominant 5-transoid rotamer.

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Substituent Interaction and Stereochemical Effects in the Electron-Impact Induced Fragmentation of N-Adamantyl Bromoamides

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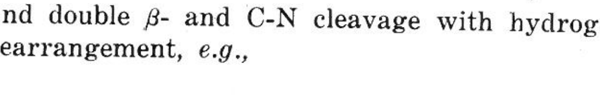
Résumé: *La fragmentation des bromo-1 adamantyl-N amides diffère de celle des amides secondaires monofonctionnels. La distance séparant les groupements fonctionnels est un facteur primordial qui détermine le processus de fragmentation. Les ions cycliques (M-Br)$^+$ sont formés avec la participation de l'azote du groupement amide lorsque la stéréochimie est favorable. On démontre qu'un réarrangement semblable à celui de Favorskii induit par un bombardement d'électrons est obtenu dans le cas des α-bromoamides.*

Abstract: *N-1-Adamantylbromoamides fragment by paths different from monofunctional secondary amides. The distance separating the functional groups is a cardinal factor determining the course of fragmentation. Cyclic (M-Br)$^+$ ions are formed where stereo-chemically favorable, with participation of the amide nitrogen. Evidence for an electron-impact induced Favorskii-like rearrangement of α-bromoamides is furnished.*

Simple monofunctional secondary amides fragment by the following major processes[1]: α-cleavage (fission of the amide bond), β-cleavage with transfer of a γ-hydrogen atom (McLafferty rearrangement) if available, double α- and C-N cleavage with hydrogen rearrangement, *e.g.*,



and double β- and C-N cleavage with hydrogen rearrangement, *e.g.*,

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