ON THE NATURE OF SIGMA-COUPLED TRANSITIONS*

THROUGH-BOND INTERACTIONS IN 1-AZA-ADAMANTANE DERIVATIVES

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Abstract – 1-Aza-adamant-4-one and a number of its derivatives, in which the CO function is modified, show absorption in the near UV region which is attributed to a sigma-coupled transition. From absorption and emission spectroscopic data it is shown that this transition has to be charge transfer in character and that it derives its intensity mainly from a local π - π * transition in the (modified) CO group. From the relative basicities, the IR spectra and the ¹³C NMR spectra it is concluded that the amount of charge transfer in the electronic ground-state is very small for the compounds studied.

INTRODUCTION

Ground-state interaction between π - or *n*-electron systems, which are spatially so far apart that direct overlap can be excluded, has been the subject of extensive research.¹⁻⁵ In recent years both calculations^{6,7} and experimental evidence³ indicate this interaction to be of the "through bond" type in which the interconnecting sigma bonds are involved. Optimal through bond interaction between two *n*-electron systems A and B which are separated by two saturated C atoms (i.e. $A - C_1 - C_2 - B$) can be expected⁸ when the lone pair orbitals on A and B are parallel to each other and to the $C_1 - C_2$ sigma bond, thus yielding the conformation depicted in Fig 1 and those obtained from it by rotation about the $C_1 - C_2$ bond.

It had been noted much earlier^{9,10} that systems fulfilling the conformational requirements outlined above but containing π -electron systems for A and/or B often show absorption bands in the near UV region which cannot be attributed to either A or B. These absorption bands have been designated as "sigma-coupled" transitions,10 implying that their occurrence involves a through bond interaction between both chromophores. Sigmacoupled transitions are observed f.i. in γ , δ unsaturated ketones and especially in β -amino ketones. There seems to be no agreement as to the nature of the sigma-coupled transition in β -amino ketones and related systems. While it has previously been described^{10, 11} as an intramolecular charge transfer transition, it has later been attributed¹² to

Part V in the series, for part IV see ref. (26); taken in part from the forthcoming thesis of A. W. J. D. Dekkers (Amsterdam 1973). the lower energy component of a split $\pi - \pi^$ transition in the CO chromophore.

One of the difficulties involved in an accurate explanation of the observed phenomena is the limited availability of suitable reference systems, possessing the required geometric properties and also sufficiently stable to permit the synthesis of electronically related derivatives. Fortunately the recently described synthetic scheme for 1-azaadamantane (1) derivatives allowed us to prepare a host of compounds in these series,¹³ several of which are eligible for a closer study of the origin of sigma-coupled transitions. The molecules under consideration are mainly derivatives (3) of 1-azaadamant-4-one, the synthesis of which is described in the experimental.

We have studied the influence of x (cf Table 1)



Fig 1. Conformation required for maximum through bond interaction between lone pair orbitals on A and B.

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Nr	x	λ ⁽¹⁾ (nm)	λ ⁽²⁾ (nm)	$ \nu_{\rm max}^{(1)} $ cm ⁻¹ ×10 ⁻³	${}^{\nu^{(2)}_{max}}_{cm^{-1} imes 10^{-3}}$	€(1) max	€ ²⁾ €max
1		211 ± 1	a	47.4 ± 0.1	a	1829	a
2a	CH ₂		—	_	_	—	
3a	CH ₂	210	—	47.6		5100	—
2b	0	_	290		34.5	—	19
3b	0	243	290 sh	41.1	34.5	1366	33
2c	$C(CN)_2$	242	_	41.3	—	12000	
3c	$C(CN)_2$	228	317	43-9	31.5	8300	4500
2d	C(CN)(COOEt)	242		41.3		14400	
3d	C(CN)(COOEt)	229	316	43.7	31.6	8780	4900
2e	CH(COOEt)	224	_	44.6	—	18150	
3e	CH(COOEt)	207	275	48.3	36.4	12630	4530
			488)		20.5)		
2f⁵	S	240	514	41.7	19.5	12700	5-10
	-		554		18.0		
			48 4)		20·7ĺ		
3f	S	322	511	31.0	19.6	(0-63)°	(<0·01)°
	~		553		18.1	,	· · ·

^aAdditional very weak transitions are observed at 280-300 nm cf ref 23.

^bValues from ref 30.

"Relative values; the instability of 3f prohibited determination of ϵ -values. 3f shows an additional band at ca 230 nm which probably consists of an $n-\sigma^*$ and the shifted $\pi-\pi^*$ transitions.

on the sigma-coupled transition in 3, which constitutes a conformationally rigid system that very nicely meets the requirements for "sigma-coupling" between the lone pair on the N atom and the π system of the C=X group (cf Fig 2).



Fig 2. 1-Aza-adamantane (1) and 1-aza-adamant-4-one (3b). In the latter the path of sigma-coupling has been indicated schematically.

RESULTS AND DISCUSSION

In Table 1 the UV spectroscopic data for 1, 2 and 3 are compiled. 3a and 3b show the expected sigma-coupled transitions at 210 and 243 nm respectively. If these transitions are charge transfer in nature with the C=X group acting as an electron acceptor, then the longer wavelength for 3b can be attributed to the higher electron affinity of the CO group relative to the vinyl group. It is well known^{14,15} that substitution of 1,1-dicyanovinyl groups for CO groups strongly enhances the electron affinity of electron acceptors. Thus 3c, d and e were synthesized with the aim of shifting the sigma-coupled transition towards longer wavelength. As can be seen from Table 1 this approach was very successful; 3c, d and e show absorption bands at 317, 316 and 275 nm respectively. Furthermore the data for model compounds 2c, d and e indicate that the C=X chromophores incorporated in these molecules display a strong $\pi - \pi^*$ transition in the near UV region. The spectra of 3c, d and e can be interpreted as consisting of the longwavelength sigma-coupled transition with in addition to this the weakened and hypsochromically shifted π - π^* transition of the C=X chromophore. The total oscillator strength of the two bands observed for 3c, d and e however approximates that of the single transition in 2c, d and e thus supporting the interpretation of the sigma-coupled transition as being one component of a split $\pi - \pi^*$ transition.

Table 1. UV absorption data as measured in n-hexane at 20°



Fig 3. Absorption spectra of 2c (....) and 3c (----) in *n*-hexane and fluorescence spectra of 3c (---) in *n*-hexane and in tetrahydrofuran.



Fig 4. Plot of fluorescence maximum observed for 3c in various solvents vs solvent polarity as expressed by Δf .

More pertinent information was gained from the fluorescence spectra of 3. While 3b is non fluorescent (its lowest excited singlet state being $n-\pi^*$ in character) 3d and especially 3c were found to display strong fluorescence upon excitation in the sigma-coupled transition. It was found that the position of this fluorescence, but not of the absorption, depends strongly on the solvent polarity (cf Fig 3). From this solvent effect we have estimated the dipole moment of the excited state for 3c, using the method employed by Knibbe¹⁶ and others.¹⁷ This method is applicable to systems for which the dipole moment of the ground state is small relative to that of the excited state ($\mu_{\rm e}$). It can be shown that

the position of the fluorescence (v_n) is then correlated to the dielectric constant (ϵ) and the refractive index (n) of the solvent by:

$$\nu_{\mathbf{n}} = \nu_{\mathbf{n}}(0) - \frac{2\mu_{\mathbf{e}}^2}{\mathbf{h}\mathbf{c}\mathbf{r}^3} \left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{4n^2 + 2}\right) =$$
$$= \nu_{\mathbf{n}}(0) - \frac{2\mu_{\mathbf{e}}^2}{\mathbf{h}\mathbf{c}\mathbf{r}^3} \Delta \mathbf{h}$$

In which $\nu_n(0)$ is the gasphase position of ν_n , h is Plancks constant, c is the velocity of light and r is the radius of the cavity formed by the solvent shell around the molecule. From a plot of ν_n versus Δf (Fig 4) the following least square fit is found:

$$\nu_{\rm fl} = (23,500) - (17,600) \,\Delta f \,({\rm cm^{-1}}) \,({\rm corr. \ coëf.} 0.975)$$

which results in:

$$\frac{\mu_{\rm e}^2}{\rm hcr^3} = 8800 \, \rm cm^{-1}$$

The molecule 3c is nonspherical but fits into an ellipsoidal cavity with a long axis of about 10 Å. According to Lippert¹⁶ one can take r to be 40% of this axis; i.e. r = 4 Å. This yields $\mu_e = 10.5$ Debye. Thus the first excited state of 3c is highly polar which strongly supports the charge transfer character of the sigma-coupled transition.

It seemed interesting to investigate whether any indication for a certain amount of charge transfer from N to C \longrightarrow X could be found in the ground state of compounds 3.

Any charge transfer was expected to lower the basicity of the N atom in 3 relative to 1. Table 2 shows that the basicity of 3b is dramatically lowered as compared to 1. It seems unlikely however that this has anything to do with a sigma-coupled charge transfer. We observe (*cf* Table 2) a comparable decrease in basicity for 5 relative to 4, while 5 is known¹⁰ to show no sigma-coupled transition because of the axial position of the N lone pair which is perpendicular to the C_{B} — C_{γ} bonds. Inductive, dipolar and especially solvation effects probably overshadow any influence of sigma-coupling on the basicities. Measurement of gasphase basicity by ioncyclotron resonance might give^{19, *} a more detailed picture of the intramolecular effects.

In principle charge transfer from N to C==X can be expected to lower the stretching vibrational frequency of the C==X double bond. For most compounds 2 and 3 however multiple bands are observed at the position of the C==X stretching frequency impeding an accurate measurement of this frequency. For 2c and 3c a single band attributable to the C==X vibration is observed at 1590.5 ± 0.5 and 1588.4 ± 0.5 cm⁻¹ respectively (chloroform solution), thus showing only a minor change.

*Measurements on aza-adamantane derivatives will be published later. ¹³C NMR shifts are known²⁰ to be very sensitive for changes in charge density. It seemed interesting to study the ¹³C NMR spectra for some of the compounds from Table 1 to see whether any indication for charge transfer could be found. The data obtained are compiled in Table 3. For 3b and 3c C₇ shows a slight upfield shift relative to 2b resp. 2c as would be expected from charge transfer towards the C=X group. However, a shift in the same direction is also observed for C₄ (cf also adamantane and 1) and no upfield shift is observed for the other carbon atoms (C₈ and C₉) of the C=X group in 3c. Thus also from the ¹³C NMR spectra no indication for a large amount of charge transfer in the ground state can be found.

From the results presented above it is concluded, that the sigma-coupled transition in 3 and related systems can mainly be described as an intramolecular charge transfer transition in which an electron is excited from the lone pair of the N atom to the first vacant level of the C=X system. In this respect it seems to be comparable with the intramolecular charge transfer transition observed by us for N-(2-arylethyl)-pyridinium ions in conformations excluding direct π - π overlap.²¹

For the C_s symmetrical compounds 3 this transition must be polarized in the mirror plane defined by C=X and N since both the donor orbital (i.e. the lone pair) and the acceptor orbital (i.e. the first vacant molecular orbital of C = X) are symmetrical (A') with respect to this plane. The charge transfer transition seems to borrow most of its intensity however from the local π - π^* transition in C==X, which is also polarized in the mirror plane (under local C_{2v} symmetry the first transition of the $C = C(CN)_2$ group was calculated by HMO to be polarized along the C=X axis). The effective intensity borrowing implies that there occurs a mixing of the N lone pair orbital with the orbitals of the C=X group.²² From the observation that the local $n-\pi^*$ transitions in the ketone **3b** and the thione 3f occur at the same frequency as those in 2b and 2f, while at the other hand the local $\pi - \pi^*$ transitions of 3(c-f) are strongly shifted relative to 2(c-f) it seems that mixing mainly occurs between the lone pair and the upper occupied π -level of C=X. This conclusion seems to be substantiated by the apparently small amount of charge transfer in the ground state.



"Handbook of Chemistry and Physics; 48th ed. (value at 25").





	δ(ppm rel. to TMS)										
Compound	Z	1	2	3	4	5	6	7	8	9	
adamantane"	СН	28.6	38.0	28.6	38.0	28.6	38.0	38.0			
1 ^b	Ν	_	59-1	33-1	36-6	33.1	59-1	36.6			
$2\mathbf{b}^a$	СН	27.7	39-1	47.1	39.1	27.7	36.6	213-1			
2b	CH	27.4	39-3	47·2	39.3	27.4	36-5	217.8	_		
3b	N		61.1	48 .0	38-1	27.0	58.3	214.3			
2c	СН	27.0	40.1	38.9	40.1	27.0	36.1	193.7	77·8	111-9	
3с	N		61.5	39.7	38.1	26.2	57.9	189.7	77.2	111-9	

^aFrom ref 24, measured in CCl₄. ^bFrom ref 25.

Our results furthermore show that systems containing the 1,1-dicyanovinyl group and related groups as an electron acceptor widen the possibilities to study the conformational dependence of through sigma bond interaction, their main advantages over the corresponding carbonyl compounds being the low energy of the sigma-coupled transitions and the local π - π * transitions as well as the applicability of the fluorescence spectroscopy.

Further research on the theoretical aspects of this interesting phenomenon and on practical applications in the conformational analysis of suitable systems is in progress.

EXPERIMENTAL

All m.ps are uncorrected. Analyses were carried out by Messr. H. Pieters of the Micro-analytical Department of this laboratory,

IR spectra were recorded on a Unicam SP 200 and Perkin-Elmer 125 and 257 spectrometers. Mass spectra were recorded on a AEI MS3-9 and a Varian MAT 711 spectrometer.

UV spectra were recorded on a Cary 14 spectrometer. Fluorescence spectra were recorded on a Zeiss spectrofluorimeter and were corrected to represent relative intensities in units of quanta per wavenumber. ¹³C Spectra were measured on a Varian XL-100 instrument and 1H NMR spectra were measured on a Varian HA 100 instrument.

1-Aza-adamantane 1,^{26,*} and 1-aza-adamant-4-methylene 3a[†] were obtained as described.

1-Aza-adamant-4-one 3b. 4-Hydroxy-aza-adamantane²⁶ (0·0495 g; 0·32 mmole) and Ag₂CO₃/Celit²⁷ (1·92 g; 3.2 mmole) in 50 ml xylene were stirred and heated at reflux. After 10 min the solid turned black. After cooling, filtration and evaporation of solvent, the white residue was purified by sublimation $(150^\circ/18 \text{ mm})$, yield: 80%. IR (CHCl₃, C==O: 1690, 1700, 1710, 1725 cm⁻¹; NMR (C₆D₈)& 2.7-3, NCH₂ (6H); 2.26 s (2H); 1.6-1.8 (4H); 1.1 s (1H). (Found: C, 71.36; H, 8.62; N, 9.31. C₉H₁₂O₁N₁. (M = 151.23). Calc: C, 71.49; H, 8.67; N, 9.26%). Mass: m/e: M⁺ = 151 (100%).

Adamantylidenemalononitrile 2c. Adamantanone, (0.3005 g; 2 mmole), malononitrile (0.1321 g; 2 mmole) and 6 drops piperidine in 50 ml benzene were stirred and heated at reflux for 6 hr (Dean Stark apparatus filled with molsieves 4A). After evaporation of solvent the residue was recrystallized twice from EtOH, yield: 0.3040 g. (76.7%), m.p. 183-185°,²⁸ IR (KBr), C=C: 1595 cm⁻¹; CN: 2240 cm⁻¹; NMR (CDCl₃)6: 3.26 s (2H); 1.7–2.3 m (12H). (Found: C, 78.75; H, 7.16; N, 14.05. C₁₃H₁₄N₂. (M = 198.29). Calc: C, 78.75; H, 7.12; N, 14.13%).

1-Aza-adamant-4-ylidenemalononitrile 3c. Compound 3b (0·3025 g; 2 mmole), malononitrile (0·1321 g; 2 mmole) and 4 drops piperidine in 50 ml benzene, were stirred and heated at reflux for 18 hr (Dean Stark apparatus, filled with molsieves 4A). After evaporation of solvent, the residue was purified twice by sublimation, (140°/11 mm), yield: 0·260 g (65%) of yellow needles, m.p.: 151-153°; IR (KBr), C=C: 1590 cm⁻¹; CN: 2250 cm⁻¹; NMR (CDCl₃)8: 2·9-3·7 m, 8H (a.o.t. CH₂N, 6H); 1·7-2·6 m (5H). (Found: C, 72·23; H, 6·67; N, 20·97. C₁₂H₁₉N₃. (M = 199·28). Calc: C, 72·33; H, 6·57; N, 21·09%).

Ethyl-adamant-2-ylidenecyanoaceiate 2d²³ ‡ was obtained as described.

Ethyl-1-aza-adamant-4-ylidenecyanoacetate 3d. Compound 3b (0.080 g; 0.53 mmole), NH₄OAc (0.050 g; 0.65 mmole), CNCH₂COOEt (0.06 ml; 0.56 mmole) and HOAc (0.1 ml; 1.6 mmole) in 5 ml benzene were stirred and heated at reflux for 20 hr (Dean Stark apparatus, filled with molsieves 4A). After cooling, the soln was extracted with H₂O. To the H₂O soln some pellets of NaOH were added and this soln was extracted with

^{*}More experimental details will be published elsewhere.

[†]Experimental details will be published later. [‡]M.p. 180–182°.

CHCl₃ 3 times. The collected organic solns were dried over Na₂SO₄. After filtration and evaporation of solvents, the residue was purified twice by sublimation (150%)11 mm), yield: 0.080g (61%), m.p. 69-72°; IR (CHCl₂), C=C: 1600 cm⁻¹; C=O: 1720 cm⁻¹; CN: 2200 cm⁻¹; NMR (CDCl₃) δ : 4·1-4·4, 3H (a.o.t. COOCH₂, q, 4·27); 2·9-3·6 m, 7H (a.o.t. CH₂N, 6H); 1·6-2·6 m (5H); 1·34 t (OCH₂CH₃). (Found: C, 68·37; H, 7·27; N, 11·25. C₁₄H₁₈O₂N₂ (M = 246·34). Calc: C, 68·27; H, 7·37; N, 11·37%.)

Ethyl-adamant-2-ylideneacetate 2c. As for the preparation of 3e, reaction time, 3 hr. After evaporation 50 ml H₂O was added to the residue. This soln was extracted 3 times with CHCl₃. The CHCl₃ soln was washed with 20 ml 0.5 N HCl and 20 ml sat NaHCO₃ aq. After drying over MgSO₄, filtration and evaporation 600 mg of oil was isolated. This was passed through a column of 9g silicagel (Woelm, activitydegree 1) with 150 ml PA 40-60/ benzene = 1:1 as an eluant. After evaporation of solvent 0.150 g (68.8%) product was obtained, m.p. 16-18°; IR (CHCl₃), C=C: 1640 cm⁻¹; C=O: 1700 cm⁻¹; NMR (CDCl₃)&: 5.58 s (C=C-H); 4-4.3 m 3H (a.o.t. O-CH₂, q, 4.13); 2.42 s (1H); 1.6-2.1 (12H); 1.26 t (O-CH₂-CH₃). (Found: C, 76-48; H, 9.09, C₁₄H₂₀O₂. (M = 220.34). Calc: C, 76.32; H, 9.15%).

Ethyl-1-aza-adamant-4-ylideneacetate 3e. To NaNH2 (0.117 g; 3 mmole) in 5 ml DMA, triethylphosphonoacetate (1 g; 4.5 mmole) in 5 ml DME was added dropwise with stirring. When the soln was clear, 3b (1 mmole) in 5 ml DME was added dropwise with stirring. The soln was stirred for 2 hr. The solvent was evaporated and water was added. Pellets of NaOH were added and the soln was extracted with CHCl₃. The extract was dried over MgSO₄. After filtration and evaporation 300 mg oil was isolated. This oil was dissolved in 2N HCl and washed 5 times with CHCl₃. The acid soln was evaporated, water and pellets of NaOH were added and this soln was extracted with CHCl₃. After drying the extract over MgSO₄, filtration and evaporation 0 150 g oil was isolated. This oil was dissolved in 10 ml benzene and 1 mmole pToSH 12 ml ether was added. A salt (oil) was formed. This was dissolved in H₂O and pellets of NaOH were added. This soln was extracted with CHCl₃. The extract was dried over MgSO4. After filtration and evaporation 0.100 g (45.2%) pure product was isolated as an oil; IR (CHCl₃), C=C: 1645 cm⁻¹; C=O: 1700 cm⁻¹; NMR (CDCl₃) δ : 5.63 s (C=C-H); 3.9-4.3 3H (a.o.t. $O - CH_2$, q, 4.14); 2.9-3.5 m (CH₂N, 6H); 1.6-2.7 m (6H); 1.26 t (COOCH₂CH₃). (Found: C, 70.39; H, 8.69; N, 6.32. $C_{13}H_{19}O_2N_1$. (M = 221.33). Calc: C, 70.55; H, 8.65; N, 6.33%).

1-Aza-adamant-4-thione 3f. Compound 3b (0.100 g; 0.66 mmole), P_2S_5 (0.222 g; 1 mmole) in 10 ml dry pyridine were stirred and heated (90°) for 18 hr. After cooling the mixture was poured out into 100 ml PA 40-60. This soln was washed with 10% Na₂CO₃ aq and with sat NaCl aq. The H₄O solns were extracted with PA 40-60. The combined PA solns were dried over MgSO₄. After filtration and evaporation 0.06 g of yellow product was isolated. This thione is very unstable and the ketone was formed back within 1 hr. In soln (*n*-hexane or PA; colour violet) in a N₂ atmosphere and in the cold the thione is more stable; IR (CHCl₃), C=S: 1145 cm⁻¹; mass: *ml*e: M⁺ = 167 (100%).

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REFERENCES

- ¹P. Bishof, J. A. Hashmall, E. Heilbronner and V. Hornung, *Helv. Chim. Acta* **52**, 1745 (1969)
- ²P. Bishof, J. A. Hashmal, E. Heilbronner and V. Hornung, *Tetrahedron Letters* 4025 (1969)
- ³E. Heilbronner and K. A. Muszkat, J. Am. Chem. Soc. 92, 3818 (1970)
- ⁴M. D. Brown, J. Hudec and J. M. Mellor, *Chem. Comm.* 1640 (1971)
- ⁶D. A. Sweigart and D. W. Turner, J. Am. Chem. Soc. 94, 5592 (1972)
- ⁶R. Hoffmann, A. Imamura and W. J. Hehre, *Ibid.* **90**, 1499 (1968)
- ⁷R. Hoffmann, Acc. Chem. Res. 4, 1 (1971)
- ⁸R. Gleiter, W. D. Stohrer and R. Hoffmann, *Helv. Chim. Acta* 55, 893 (1972).
- ⁹K. Wiesner, H. W. Brewer, D. L. Simmons, D. R. Babin, F. Bickelhaupt, J. Kallos and T. Bogri, *Tetrahedron Letters* 17 (1960).
- ¹⁰R. C. Cookson, J. Henstock and J. Hudec, J. Am. Chem. Soc. 88, 1061 (1966)
- ¹¹J. Kuthan, J. Palecek and L. Musil, Z. Chem. 8, 229 (1968)
- ¹²J. Hudec, Chem. Comm. 829 (1970)
- ¹³J. Dijkink and W. N. Speckamp, to be published
- ¹⁴T. K. Mukherjee and L. A. Levasseur, J. Org. Chem. **30**, 644 (1965)
- ¹⁵S. Chatterjee, J. Chem. Soc. (B), 725 (1969)
- ¹⁶H. Knibbe, Thesis, Free University of Amsterdam (1969)
- ¹⁷T. Okada, T. Fujita, M. Kubota, S. Masaki, N. Mataga, R. Ide, Y. Sakata and S. Misumi, *Chem. Phys. Lett.* 14, 563 (1972)
- ¹⁸E. Lippert, Zt. Elektrochem. Ber. Bunsen Ges. 61, 962 (1957)
- ¹⁹D. H. Aue, H. M. Webb and M. T. Bowers, J. Am. Chem. Soc. 94, 4726 (1972)
- ²⁰G. A. Olah and A. M. White, Ibid. 91, 5801 (1969)
- ²¹J. W. Verhoeven, I. P. Dirkx and Th. J. de Boer, J. Mol. Spectr. **42**, 149 (1972)
- ²²J. N. Murrell, The Theory of the Electronic Spectra of Organic Molecules. Methuen, London (1963)
- ²³A. Halpern, to be published
- ²⁴T. Pehk, E. Lippmaa, V. V. Sevostjanova, M. M. Krayuschkin and A. I. Tarasova, Org. Magn. Res. 3, 783 (1971)
- ²⁵I. Morishima, K. Okada, T. Yonezawa and K. Goto, J. Am. Chem. Soc. 93, 3922 (1971)
- ²⁶W. N. Speckamp, J. Dijkink and H. O. Huisman, Chem. Comm. 197 (1970).
- ²⁷M. Fetizon and M. Golfier, Cr. Acad. Sci. Paris, 267c, 900 (1968)
- ²⁸R. v. Hes, A. Smit, T. Kralt and A. Peters, J. of Medicinal Chem. 15, 132 (1972)
- ²⁹K. Lundahl, J. Schut, J. L. M. A. Schlatmann, G. B. Paerels and A. Peters, J. of Medicinal Chem. 15, 129 (1972)
- ³⁰J. W. Greidanus, Canad. J. Chem. 48, 3530 (1970)