

THE ASTROBIOLOGY OF NUCLEOBASES

Z. PEETERS AND O. BOTTA

Astrobiology Laboratory, Leiden Institute of Chemistry, P.O. Box 9502, 2300 RA Leiden, The Netherlands

S. B. CHARNLEY

Space Science Division, NASA Ames Research Center, MS 245-3, Moffett Field, CA 94035

AND

R. RUITERKAMP AND P. EHRENFREUND

Leiden Observatory, P.O. Box 9513, 2300 RA Leiden, The Netherlands

Received 2003 May 9; accepted 2003 July 11; published 2003 July 29

ABSTRACT

Nucleobases are nitrogen heterocycles (N-heterocycles) that are essential components of the genetic material in all living organisms. Extraterrestrial nucleobases have been found in several carbonaceous chondrites, but only in traces. No astronomical data on these complex molecules are currently available. A large fraction of the cosmic carbon is known to be incorporated into aromatic material, and given the relatively high abundance of cosmic nitrogen, the presence of N-heterocycles can be expected. We present infrared spectroscopic laboratory data of adenine and uracil under simulated space conditions. At the same time we tested the stability of these nucleobases against ultraviolet (UV) irradiation at 12 K. Our experimental results indicate that gas-phase adenine and uracil will be destroyed within hours in the Earth's vicinity. In dense interstellar clouds exposed to UV radiation, only adenine could be expected to survive for a few million years. We discuss possible formation routes to purines and pyrimidines in circumstellar environments and in meteorite parent bodies.

Subject headings: circumstellar matter — meteors, meteoroids — methods: laboratory

1. INTRODUCTION

Many complex organic molecules have been detected in the interstellar medium (ISM) and in solar system objects in the solid state or dispersed in the gas phase (see Ehrenfreund & Charnley 2000 for a review). The dominant fraction of cosmic carbon is incorporated in aromatic material, likely in gaseous polycyclic aromatic hydrocarbons (PAHs) and in the solid aromatic networks that comprise carbonaceous dust. The ubiquitous signatures of aromatic material visualized by infrared emission bands between 3 and 15 μm also provide evidence for the presence of five-membered ring structures and attached side groups (Tielens et al. 1999). Nucleobases such as purines and pyrimidines are small N-containing aromatic ring structures that play a major role in terrestrial biochemistry. They are central components of DNA and RNA, molecules that are used in the storage, transcription, and translation of genetic information. At present, extraterrestrial N-heterocycles have been detected only in carbonaceous meteorites (Stoks & Schwartz 1979, 1981).

In this Letter we report experimental results on the spectroscopy and photostability of adenine and uracil. We also evaluate possible nucleobase formation mechanisms in a variety of astronomical environments.

2. WHERE COULD NUCLEOBASES BE FORMED IN SPACE?

There are several tentative formation routes of nucleobases in interstellar, circumstellar, and solar system environments. Currently there are no astronomical data available to identify nucleobases in interstellar or circumstellar environments. Theoretical scenarios for the interstellar formation of prebiotic compounds in the ISM have most recently been discussed by Charnley et al. (2001), Chakrabarti & Chakrabarti (2000), Hollis & Churchwell (2001), and Sorrell (2001). Chakrabarti & Chakrabarti (2000) suggested a gas-phase formation of adenine in molecular clouds. However, this route to the formation of

nucleobases in dense molecular clouds and star-forming cores can be ruled out on the basis of the calculations of Smith et al. (2001). The computed rate coefficient for HCN dimerization, the first step on the proposed formation route of Chakrabarti & Chakrabarti (2000), is $\sim 10^{-10} \exp(-36,000/T) \text{ cm}^3 \text{ s}^{-1}$ and implies that adenine formation will not occur in such regions, where temperatures are in the range of $T \sim 10\text{--}300 \text{ K}$. Also, adenine could be formed in the inner circumstellar envelopes of C stars ($T \sim 1000\text{--}1500 \text{ K}$), where formation of aromatic compounds is known to occur (Frenklach & Feigelson 1989). In this case, N-heterocycles may form as by-products of the acetylene polymerization which leads to large PAH molecules.¹

Intermediate HCN additions could lead to direct incorporation of nitrogen atoms into growing aromatic rings (Ricci et al. 2001). For example, in the initial stage of ring closure to form a phenyl radical ($\text{C}_6\text{H}_5 \cdot$), an HCN addition, instead of an acetylene addition, will lead to the formation of pyridine. Similarly, the replacement of an acetylene by an HCN during the subsequent formation of naphthalene would lead to isoquinoline. Molecules formed in this scenario will preferentially contain one nitrogen atom per aromatic ring rather than several nitrogen atoms in one ring as in adenine, making this mechanism an inefficient source of adenine. The presence of two oxygen side groups in uracil rules out its formation in C star atmospheres.

Irradiation of PAH molecules embedded in H_2O ice matrices leads to the formation of various carbonyl compounds such as quinones and ethers (Bernstein et al. 1999). However, these experiments showed no inclusion of oxygen into the aromatic ring structure of the PAHs; side group additions are preferred (Bernstein et al. 2003). The situation is unknown for irradiation of PAHs in nitrogen-rich ices, but a highly efficient mechanism would have to operate to produce such a nitrogen-rich molecule

¹ Note that HCN dimerization in these environments is also ruled out by the calculations of Smith et al. (2001).

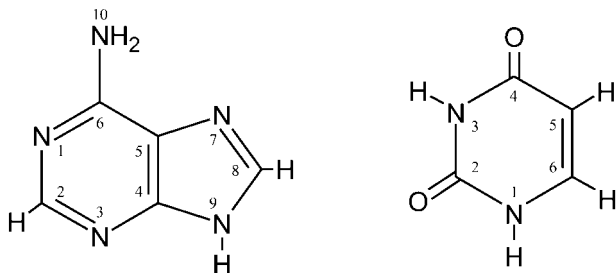


FIG. 1.—Structural formulae of adenine (left, $C_5H_5N_5$) and uracil (right, $C_4H_4N_2O_2$).

as adenine. Irradiation of interstellar pyrimidine ($c-C_4H_4N_2$) in water ice could possibly produce the necessary side group additions for uracil. However, existing upper limits on the abundance of interstellar pyrimidine (Kuan et al. 2003b) tend to greatly constrain the amount of pyrimidine available for this synthesis. For both adenine and uracil, the experimental data reported in this Letter limit the possibility that these molecules can survive in environments where a significant UV flux is present.

As traces of nucleobases have been identified in carbonaceous meteorites, the formation of nucleobases within the solar system appears to be more promising. No isotopic measurements have been made for any N-heterocyclic compound found in meteorites that would provide definitive evidence for their extraterrestrial origin. However, on the basis of the very low contamination levels of amino acids in these meteorites, a low terrestrial contamination for the nucleobases can be inferred. Indigenous purines and pyrimidines have been detected in several carbonaceous chondrites. The pyrimidine uracil and the purines adenine, guanine, xanthine, and hypoxanthine (Stoks & Schwartz 1979, 1981) were detected in the CM carbonaceous chondrites Murchison and Murray, as well as in the CI meteorite Orgueil, in total concentrations of about 1.3 parts per million (ppm). Upper limits exist (detection limit of 0.01 ppm) for the concentrations of thymine and cytosine, as well as other heterocyclic compounds, in the Murchison meteorite (van der Velden & Schwartz 1977).

The synthetic pathways for the formation of nucleobases in a meteoritic parent body might be similar to those suggested for their prebiotic formation on the early Earth. In this scenario stepwise oligomerization of HCN leads to the formation of the tetramer diaminomaleonitrile (DAMN). Subsequent steps lead to the formation of 4-aminoimidazole-5-carbonitrile (AICN) (Ferris & Hagan 1984). This intermediate can react either with HCN to form adenine and hypoxanthine or with urea to form guanine and xanthine. All these reactants are potential prebiotic compounds; however, only HCN has been identified in the ISM and in comets.

3. EXPERIMENTAL

Matrix isolation spectroscopy and subsequent UV destruction of adenine and uracil (see Fig. 1) was carried out using techniques described elsewhere (Ehrenfreund et al. 2001). For the matrix material, 99.999% pure argon (Praxair) was used. Adenine (purity of 99%) was purchased from Merck, and uracil (purity of 98%) was purchased from Sigma. The nucleobase samples were sublimed from a furnace at 100°C onto a 12 K CsI window. Simultaneously, the matrix gas was deposited onto the window from a separate inlet port at a rate of 3.0×10^{19}

TABLE 1
DESTRUCTION CROSS SECTIONS AND HALF-LIFETIMES FOR THE
NUCLEOBASES AND GLYCINE

COMPOUND	σ_{uv} (cm^2 per molecule)	HALF-LIFETIME			
		Lab (s)	DISM (yr)	DC (Myr)	1 AU (s)
Adenine	2.7×10^{-18}	518	82.7	8.27	8654
Uracil	1.1×10^{-17}	127	20.3	2.03	2120
Glycine	1.2×10^{-17}	115	18.4	1.84	1925

NOTE.—This table lists the destruction cross section and half-lifetimes for the nucleobases and glycine in different environments. The destruction cross section was calculated by monitoring the disappearance of infrared transitions in Figs. 2 and 3. The half-lifetimes were subsequently calculated using the specific UV flux for the given environment (see the text).

molecules $cm^{-2} hr^{-1}$ or $11.3 \mu m hr^{-1}$. The column densities of adenine and uracil were estimated from the most prominent bands. The mode descriptions and associated band strengths were taken from Nowak et al. (1996) for adenine and from Leś et al. (1992) for uracil. The nucleobase to argon ratio in the resulting matrix was approximately 1 : 1500.

UV irradiation was performed using a microwave-excited hydrogen flow lamp with a flux ϕ of 5×10^{14} photons $s^{-1} cm^{-2}$, calibrated according to the method described by Gerakines et al. (2000). Photodestruction of the nucleobase samples was monitored by in situ Fourier transform infrared spectroscopy using an Excalibur FTS-4000 (BioRad) at $1 cm^{-1}$ resolution. Column densities were calculated from integrated peaks and plotted against time. These data were fitted with the function $N_0 e^{-kt}$, where N_0 is the initial (before photolysis) column density in molecules cm^{-2} and t is the time of irradiation in seconds, yielding the destruction rate constant k in s^{-1} . Furthermore $k = \sigma_{uv}\phi$, where σ_{uv} is the UV destruction cross section in $cm^2 molecule^{-1}$. Finally, half-lifetimes—defined as the amount of time required to destroy 50% of the starting material—were calculated for different environments, using the known UV fluxes for laboratory conditions, the diffuse interstellar medium (DISM, 1×10^8 photons $cm^{-2} s^{-1}$; Mathis et al. 1983), dense clouds (DCs, 1×10^3 photons $cm^{-2} s^{-1}$; Prasad et al. 1983), and the Sun at 1 AU (3×10^{13} photons $cm^{-2} s^{-1}$); see Table 1.

4. RESULTS AND DISCUSSION

The UV destruction of adenine and uracil in solid Ar at 12 K was measured by monitoring the disappearance of spectral features associated with specific molecular functional groups. For adenine the relevant bands are found at $3557 cm^{-1}$ (NH_2), $3498 cm^{-1}$ [$N(9)H$], $3441 cm^{-1}$ (NH_2), $1651-1599 cm^{-1}$ ($C=C$, $C=N$), $1474 cm^{-1}$ ($C=N$, $C-H$), $1290 cm^{-1}$ ($C=N$), and $803 cm^{-1}$ (ring mode). Figure 2 shows the degradation of adenine upon photolysis in defined time steps of 1, 10, and 30 minutes, after which nearly all bands have disappeared. Photoproducts identified at 904 and $1092 cm^{-1}$ have been tentatively assigned to HAr_n^+ (Milligan & Jacox 1973) and the ν_3 absorption of HO_2 (Jacox & Milligan 1972), respectively; these may result from residual water contamination in the setup. No likely candidate could be identified for a third feature that appeared at $1141 cm^{-1}$.

Figure 3 shows the destruction of the pyrimidine compound uracil. The functional group specific signals of uracil are at $3485 cm^{-1}$ [$N(1)H$], $3435 cm^{-1}$ [$N(3)H$], $1792-1681 cm^{-1}$ ($C=O$), $1399 cm^{-1}$ ($N-H$, $C-N$), $1185 cm^{-1}$ ($C-H$, $N-H$), $804 cm^{-1}$ [$C(4)O$, $C(5)H$], and $757 cm^{-1}$ [$C(2)O$]. After 20

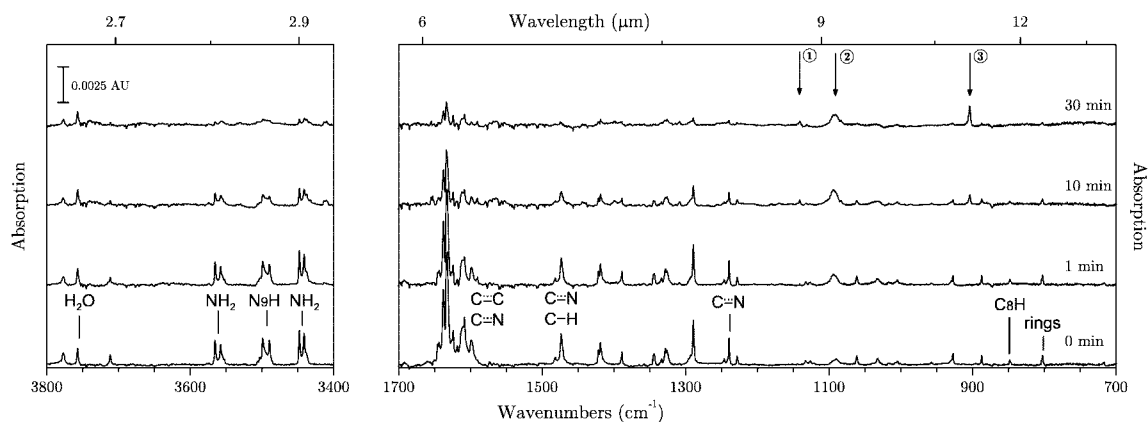


FIG. 2.—Infrared spectra of adenine isolated in argon (1 : 1500) at 12 K in the ranges 3800–3400 and 1700–700 cm^{-1} (AU = absorption units). The major infrared transitions are labeled. The spectra were recorded after deposition (0 minutes) and 1, 10, and 30 minutes of exposure to UV radiation. The peaks that emerge after UV photolysis are depicted with arrows, labeled “1” at 1141 cm^{-1} , “2” at 1093 cm^{-1} , and “3” at 904 cm^{-1} .

minutes of irradiation all uracil-specific peaks disappeared while new peaks emerged at 904, 1092, 1141, 2143, 2263, and 2345 cm^{-1} . The first three peaks have the same tentative assignment as for the adenine photolysis. The peaks at 2143 and 2345 cm^{-1} are the well-described stretching modes of CO and CO_2 , respectively. The band at 2263 cm^{-1} is tentatively ascribed to the ν_2 absorption of HNCO (Bondybey et al. 1982). Isolated water bands around 3700 cm^{-1} are marked in Figures 2 and 3. The water content has been estimated from those bands using the cross sections given by Redington & Milligan (1962) and has been assessed to be negligible, namely, 4.0×10^{14} molecules cm^{-2} . The UV radiation has been performed in a careful experimental procedure ensuring that the sample thickness of the Ar layer does not exceed 1 μm , allowing full penetration of all UV photons throughout the ice layer. From the structural formula of uracil it seems apparent that by breaking the bonds between C(2) and N(3), between C(4) and C(5), and between C(6) and N(1) (see Fig. 1), photolysis would yield two HNCO molecules per uracil, which are identified by the 2263 cm^{-1} band in the spectrum. The remainder could then form acetylene (C_2H_2). However, no acetylene was found in the matrix. For adenine, no infrared active photolysis products were found. The exact degradation routes for both adenine and uracil will be investigated in future research.

From the disappearance of the major features in the adenine and uracil spectra over time, half-lifetimes were calculated for several different environments. The results are listed in Table 1. Also incorporated in Table 1 is the half-lifetime for the amino acid glycine. The photostability of glycine measured in this experiment is lower than previously measured by Ehrenfreund et al. (2001). The current values are believed to be more accurate owing to the controlled thin sample thickness in our experiments. The stability of uracil was found to be rather low, only slightly higher than glycine. Adenine, however, showed a stability against UV irradiation 5 times higher than that of glycine. In contrast to the efficient photodestruction nucleobases undergo, larger N-substituted PAHs exhibit much greater photostability and can become photoionized (Mattioda et al. 2003). This means that any ionization products in our experiments cannot be effectively monitored and will make only a minor contribution to the loss of IR absorption.

The experimental data for argon matrices provide upper limits for the survival of nucleobases in specified regions of space. From Table 1 it is clear that even if nucleobases are formed around evolved stars, they could not survive in the diffuse interstellar medium for more than several hundred years. Near the Earth, at 1 AU from the Sun, adenine and uracil would be destroyed in a matter of hours. The average lifetime of shielded

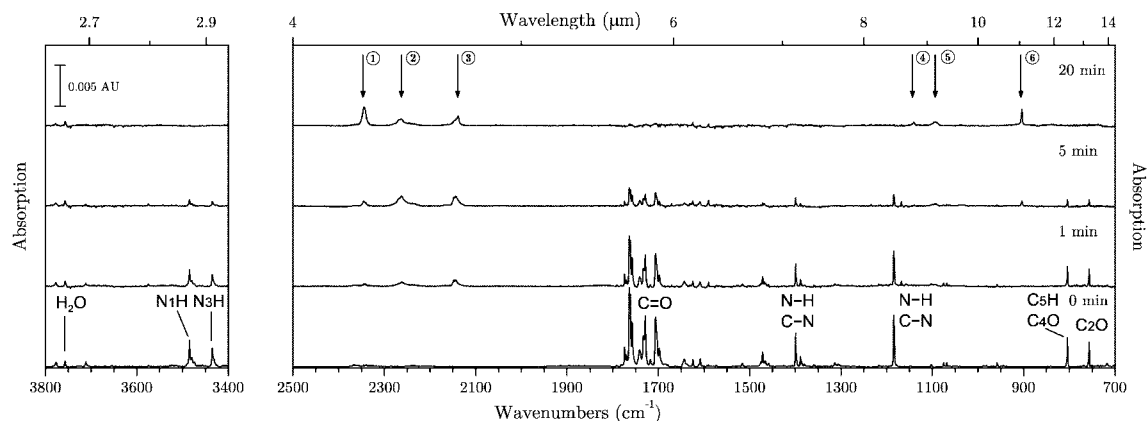


FIG. 3.—Infrared spectra of uracil isolated in argon (1 : 1500) at 12 K in the ranges 3800–3400 and 2500–700 cm^{-1} (AU = absorption units). The major infrared transitions are labeled. The spectra were recorded after deposition (0 minutes) and 1, 5, and 20 minutes of exposure to UV radiation. The peaks that emerge after UV photolysis are depicted with arrows, labeled “1” at 2345 cm^{-1} , “2” at 2263 cm^{-1} , “3” at 2143 cm^{-1} , “4” at 1141 cm^{-1} , “5” at 1093 cm^{-1} , and “6” at 904 cm^{-1} .

environments like molecular clouds is uncertain. Short cloud lifetimes of $\sim 1\text{--}3$ Myr (e.g., Elmegreen 2000; Hartmann et al. 2001) favor the survival of all three molecules. For longer lifetimes of ~ 10 Myr, only adenine could be expected to survive over a significant fraction of a cloud's life, e.g., over the age of the Taurus cloud complex (~ 6 Myr; Cohen & Kuhl 1979).

5. CONCLUSIONS

Taking into account our current understanding of the relevant chemistry, it is doubtful that nucleobase formation can proceed efficiently in circumstellar and interstellar environments. Although the photostability of adenine is a factor of 5 larger than for uracil and glycine, it is still sufficiently low to limit its lifetime in such environments. Their instability against UV photons also implies that photochemical production on the surface of interstellar grains will be inefficient.

The detection of glycine in Sgr B2 (N), Orion, and W51 e1/e2 by Kuan et al. (2003a) supports the idea that formation of simple amino acids can proceed via gas-phase reactions (Charnley et al. 2001) in the UV-shielded environment of hot

cores. In the case of nucleobases, it seems most likely that they can be formed only in the solar system, where they could be readily synthesized from common extraterrestrial starting materials such as hydrogen cyanide and cyanoacetylene (Ferris & Hagan 1984). Ideal environments in which to form nucleobases such as adenine and uracil are the parent bodies of meteorites. Comets may also be a formation site if HCN polymerization is invoked. The formed nucleobase compounds could then be protected from UV photons in cometary subsurface layers. Their survival time in the solar system is extremely limited when unprotected against UV radiation, only several hours in the vicinity of the Earth. It can be concluded that the precursors of terrestrial biomolecules, such as amino acids and nucleobases, are not very resistant against UV radiation and that these compounds require protective conditions for them to be formed, transported, and delivered to the early planets.

This work was supported by VI (Verniewingsimpuls, NWO) and NASA's Exobiology Program through NASA Ames Interchange NCC2-1162.

REFERENCES

- Bernstein, M. P., Moore, M. H., Elsila, J. E., Sandford, S. A., Allamandola, L. J., & Zare, R. N. 2003, *ApJ*, 582, L25
- Bernstein, M. P., Sandford, S. A., Allamandola, L. J., Gillette, J. S., Clemett, S. J., & Zare, R. N. 1999, *Science*, 283, 1135
- Bondybey, V. E., English, J. H., Weldon Mathews, C., & Contolini, R. J. 1982, *J. Mol. Spectrosc.*, 92, 431
- Chakrabarti, S., & Chakrabarti, S. K. 2000, *A&A*, 354, L6
- Charnley, S. B., Ehrenfreund, P., & Kuan, Y.-J. 2001, *Spectrochim. Acta A*, 57, 685
- Cohen, M., & Kuhl, L. W. 1979, *ApJS*, 41, 743
- Ehrenfreund, P., Bernstein, M. P., Dworkin, J. P., Sandford, S. A., & Allamandola, L. J. 2001, *ApJ*, 550, L95
- Ehrenfreund, P., & Charnley, S. B. 2000, *ARA&A*, 38, 427
- Elmegreen, B. G. 2000, *ApJ*, 530, 277
- Ferris, J. P., & Hagan, W. J. 1984, *Tetrahedron*, 40, 1093
- Frenklach, M., & Feigelson, E. 1989, *ApJ*, 341, 372
- Gerakines, P. A., Moore, M. H., & Hudson, R. L. 2000, *A&A*, 357, 793
- Hartmann, L., Ballesteros-Paredes, J., & Bergin, E. A. 2001, *ApJ*, 562, 852
- Hollis, J. M., & Churchwell, E. 2001, *ApJ*, 551, 803
- Jacox, M. E., & Milligan, D. E. 1972, *J. Mol. Spectrosc.*, 42, 495
- Kuan, Y.-J., Charnley, S. B., Huang, H.-C., Tseng, W.-L., & Kisiel, Z. 2003a, *ApJ*, 593, 848
- Kuan, Y.-J., Yan, C.-H., Charnley, S. B., Kisiel, Z., Ehrenfreund, P., & Huang, H.-C. 2003b, *MNRAS*, in press
- Leś, A., Adamowicz, L., Nowak, M. J., & Lapinski, L. 1992, *Spectrochim. Acta A*, 48, 1385
- Mathis, J. S., Mezger, P. G., & Panagia, N. 1983, *A&A*, 128, 212
- Mattioda, A. L., Hudgins, D. M., Bauschlicher, C. W., Rosi, M., & Allamandola, L. J. 2003, *J. Phys. Chem. A*, 107, 1486
- Milligan, D. E., & Jacox, M. E. 1973, *J. Mol. Spectrosc.*, 46, 460
- Nowak, M. J., Lapinski, L., Kwiatkowski, J. S., & Leszczynski, J. 1996, *J. Phys. Chem.*, 100, 3527
- Prasad, S., & Tarafdar, S. P. 1983, *ApJ*, 267, 603
- Redington, R. L., & Milligan, D. E. 1962, *J. Chem. Phys.*, 37, 2162
- Ricci, A., Bauschlicher, C. W., & Bakes, E. L. O. 2001, *Icarus*, 154, 516
- Smith, I. W. M., Talbi, D., & Herbst, E. 2001, *A&A*, 369, 611
- Sorrell, W. H. 2001, *ApJ*, 555, L129
- Stoks, P. G., & Schwartz, A. W. 1979, *Nature*, 282, 709
- . 1981, *Geochim. Cosmochim. Acta*, 45, 563
- Tielens, A. G. G. M., Hony, S., van Kerckhoven, C., & Peeters, E. 1999, in *The Universe as Seen by ISO*, ed. P. Cox & M. F. Kessler (ESA SP-427; Noordwijk: ESA), 579
- Van der Velden, W., & Schwartz, A. W. 1977, *Geochim. Cosmochim. Acta*, 41, 961