

## Kurzmitteilung / Short Communication

# Mass-Spectrometric Characterization of Isomeric NNCCN and NCNCN Ions and Neutrals

César A. Muedas, Detlev Sülzle<sup>[\*]</sup>, and Helmut Schwarz\*

Institut für Organische Chemie der Technischen Universität Berlin,  
Straße des 17. Juni 135, W-1000 Berlin 12, F.R.G.

Received March 30, 1992

**Key Words:** Interstellar chemistry / Heterocumulenes / Charge-reversal mass spectrometry / Neutralization-reionization mass spectrometry / Collisional activation

Neutralization-reionization mass spectrometry as well as charge reversal and collisional activation experiments serve to distinguish and assign the connectivities NNCCN and NCNCN to isomeric pairs of anions, neutral radicals and cat-

ions of  $C_2N_3$ . Loss of  $N_2$  to generate  $C_2N^+$  is the critical discriminant, and the assignment is further substantiated by subjecting these fragment ions to collisional activation experiments by using tandem-mass spectrometry facilities.

Recent work in our laboratory has dealt with the study of cumulenes of cosmochemical and theoretical relevance<sup>[1]</sup>. Particularly challenging is the prospect of distinguishing isomeric structures in heteroatom-containing species. The use of tandem-mass spectrometry is once again utilized in this report for the characterization of two isomers of  $C_2N_3$ , namely NNCCN and NCNCN as such neutrals and their corresponding cations and anions in the gas phase.

### Results and Discussion

Scheme 1 depicts our approach to the generation of two isomers of  $C_2N_3$  in our tandem mass spectrometer. The formation of di-

Scheme 1

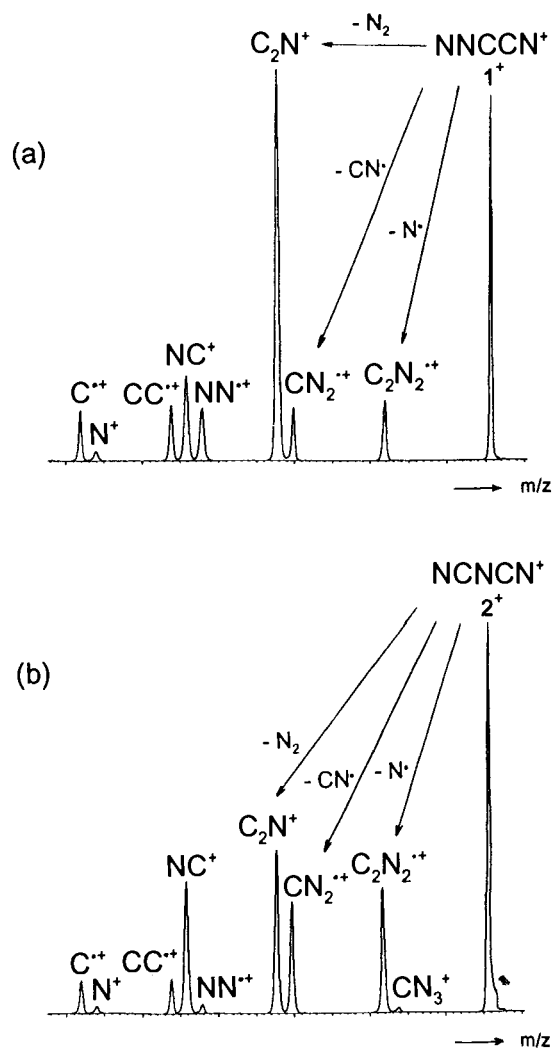
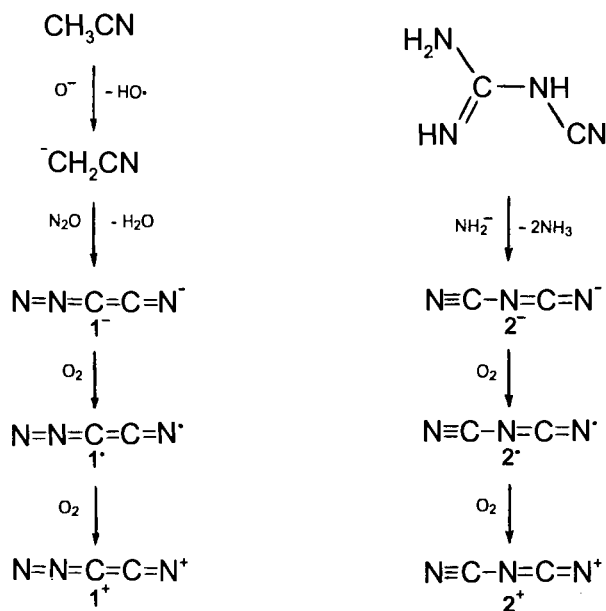


Figure 1. CR mass spectra of: a)  $C_2N_3^-$  from deprotonation and diazotization of  $CH_3CN$ ; b)  $C_2N_3^-$  from deprotonation and deamination of cyanoguanidine

[\*] Present address: Schering AG, Postfach 650311, W-1000 Berlin 65, F.R.G.

azocyanomethanide ( $1^-$ ) is a straightforward diazotization reaction typical of a primary carbanion<sup>[2]</sup>. On the other hand, cyanoguanidine behaves as a suitable precursor for dicyanomethanide ( $2^-$ ) when treated with ammonia in the ion source, i.e., collisions with the reagent gas result in concomitant deprotonation and deamination (for details, see Experimental).

Each anion of  $m/z = 66$  is mass-selected from the source by double-focusing and submitted to charge reversal (CR)<sup>[3]</sup>. The corresponding cations render the fragmentation patterns shown in Figure 1. Clear differences are observable in the relative intensities of the fragment peaks, most pronounced for the loss of dinitrogen leading to  $m/z = 38$  [ $C_2N^+$ ] and in the abundance of  $m/z = 28$  [ $N_2^+$ ]. A minor, though distinct feature is the weak signal at  $m/z = 54$  [ $CN_3^+$ ] arising from  $NCNCN^+$  exclusively.

Both  $1^-$  and  $2^-$  undergo efficient neutralization and reionization to their cations ( $^-NR^+$  experiments)<sup>[4]</sup>. The NR spectra (Figure 2), vis-à-vis the CR ones, establish the correspondence of identical connectivities for each anion/radical/cation set. The noticeable intensity of the recovery signals supports the existence of the radicals  $1^\cdot$  and  $2^\cdot$  as solitary species in the gas phase within the timescale of the  $^-NR^+$  measurements (ca. 1  $\mu$ s).

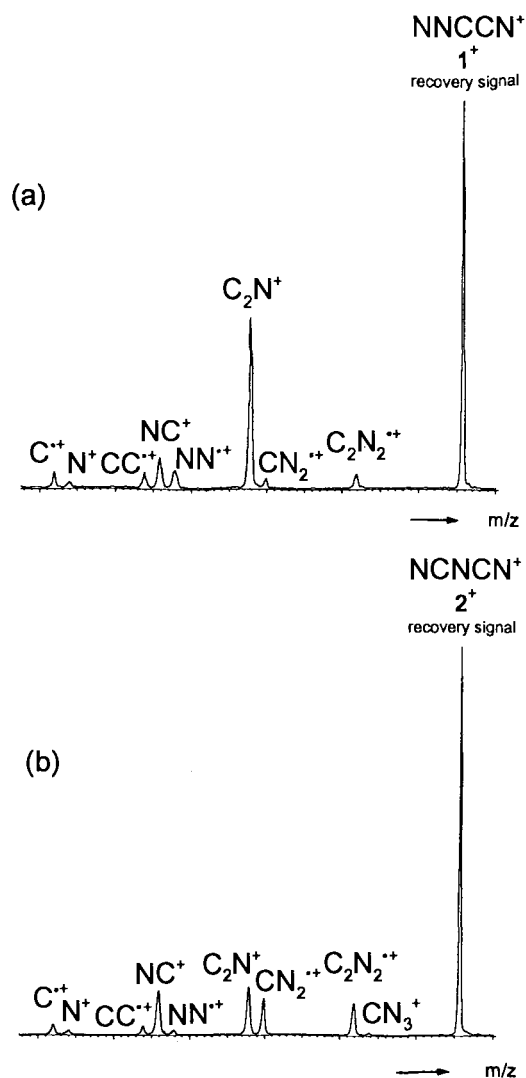


Figure 2.  $^-NR^+$  mass spectra of (a)  $NNCCN^-$  ( $1^-$ ) and (b)  $NCNCN^-$  ( $2^-$ )

Complementary evidence for the assignment of structures  $NNCCN$  and  $NCNCN$  (ions and neutrals) is provided by collisional activation (CA) analysis of isobaric fragment ions selected from the CR experiment, i.e., CR/CA experiments.

Starting from  $1^-$ , the ion  $C_2N_2^+$  ( $m/z = 52$ ) can be due to  $NNCC^+$  or  $NCCN^+$ ; from  $2^-$ , however,  $m/z = 52$  should be  $NCNC^+$ . As the spectra in Figure 3 show, the intensity of  $CC^+$  is markedly higher coming from  $NNCC^+$  or  $NCCN^+$  (Figure 3a) where the  $CC$  moiety is already present. Similarly, we note the intensive signal for  $NN^+$  in Figure 3a as compared with Figure 3b. Interestingly, the signal for  $CC^+$  from  $NCNC^+$  points to significant structural reorganization prior to dissociation. This observation is in agreement with a previous report on the abundant loss of  $N_2$  from  $NCNC^+$ <sup>[5]</sup>.

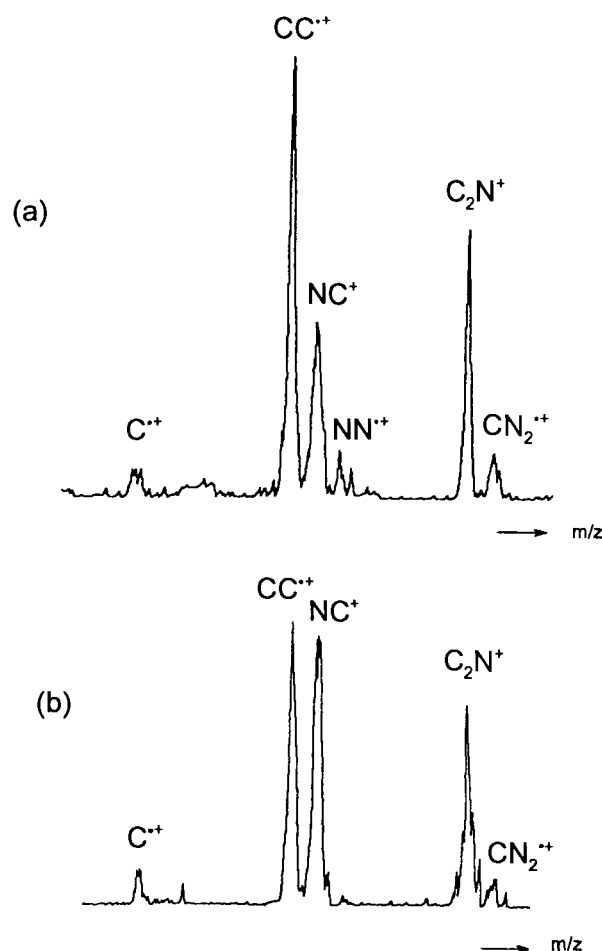


Figure 3. CR/CA mass spectra of isomeric  $C_2N_2^+$  ions generated from (a)  $NNCCN^-$  ( $1^-$ ) and (b)  $NCNCN^-$  ( $2^-$ ) by loss of an N atom

Selection and analysis of  $m/z 40$  [ $CN_2^+$ ] reveals the difference between  $NNC^+$  and  $NCN^+$  (Figure 4). The former ion is predicted to display a strong signal for  $N_2^+$ , as is the case for its parent ion  $NNCCN^+$ . This is indeed borne out in Figure 4a. Even if  $CN_2^+$  is in each case a mixture, the different intensities for  $N_2^+$  are consistent with  $CN_2^+$  originating in distinct isomers, one of which does contain a prevalent N–N connectivity.

The fragmentation of  $m/z = 38$  [ $C_2N^+$ ] (Figure 5) is identical irrespective of the starting parent ion  $1^-$  or  $2^-$ . This result aids on the explanation of how extrusion of  $N_2$  may occur, i.e.,  $C_2N^+$  must

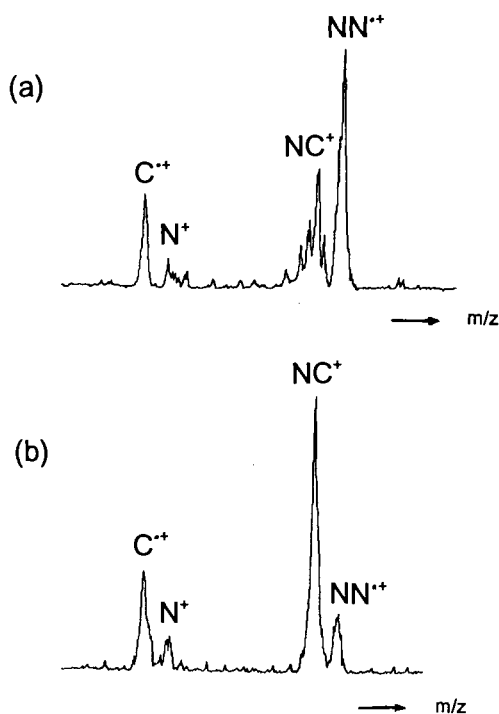


Figure 4. CR/CA mass spectra of isomeric  $\text{CN}_2^+$  ions generated from (a)  $\text{NNCCN}^- (1^-)$  and (b)  $\text{NCNCN}^- (2^-)$  by loss of  $\text{CN}^+$

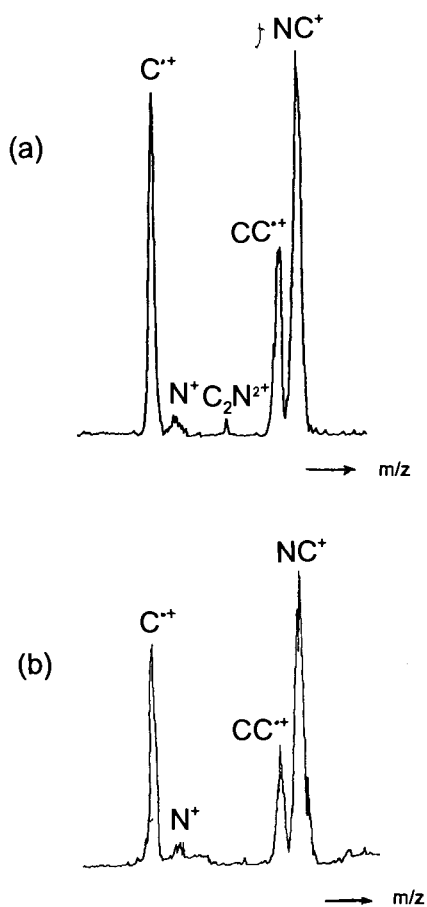


Figure 5. CR/CA mass spectra of isomeric  $\text{C}_2\text{N}^+$  ions generated from (a)  $\text{NNCCN}^- (1^-)$  and (b)  $\text{NCNCN}^- (2^-)$  by loss of  $\text{N}_2$

consist in both cases of the same contributors ( $\text{CCN}^+$  and  $\text{CNC}^+$ , or identical mixtures of these two). The isomer  $\text{NNCCN}^+$ , regardless of the way  $\text{N}_2$  is eliminated, can give rise to  $\text{CCN}^+$  only, and therefore  $\text{CCN}^+$  must be the major component in  $m/z = 38$ . Consequently, the formation of  $\text{CCN}^+$  from  $\text{NCNCN}^+$ , will necessarily involve a formal 1,3-elimination of  $\text{N}_2$  as the major pathway. Moreover, "clean"  $\text{CCN}^+$  has been characterized in CR/CA experiments on  $\text{NCCCN}^-$  and does present exactly the same pattern as in the fragmentation of  $\text{C}_2\text{N}^+$  here observed<sup>[6]</sup>. Therefore, we propose that additional, not yet fully understood decomposition pathways are operative in the  $\text{N}_2$  dissociation from  $1^-$  and  $2^-$  under CR conditions.

A third precursor to  $\text{C}_2\text{N}_3^-$  was also found in 1*H*-1,2,4-triazole. CR and  $^- \text{NR}^+$  experiments were similarly performed as above. The spectra (Figure 6) point to  $m/z = 66$ , in this case, as being nearly identical to  $\text{NCNCN}^-$  ions and radical. The differences may be attributed to an  $\text{NCNCN}^-$  in an electronic state different from that of  $2^-$ . In fact, this occurrence is limited to the CR experiment as the  $^- \text{NR}^+$  spectra given in Figures 2b and 6b are identical, i.e., notwithstanding the electronic state in which  $\text{NCNCN}^-$  is generated, the neutral is cool and long-lived enough to be always reionized to  $\text{NCNCN}^+$  by identical channels. The weakness of the iso-

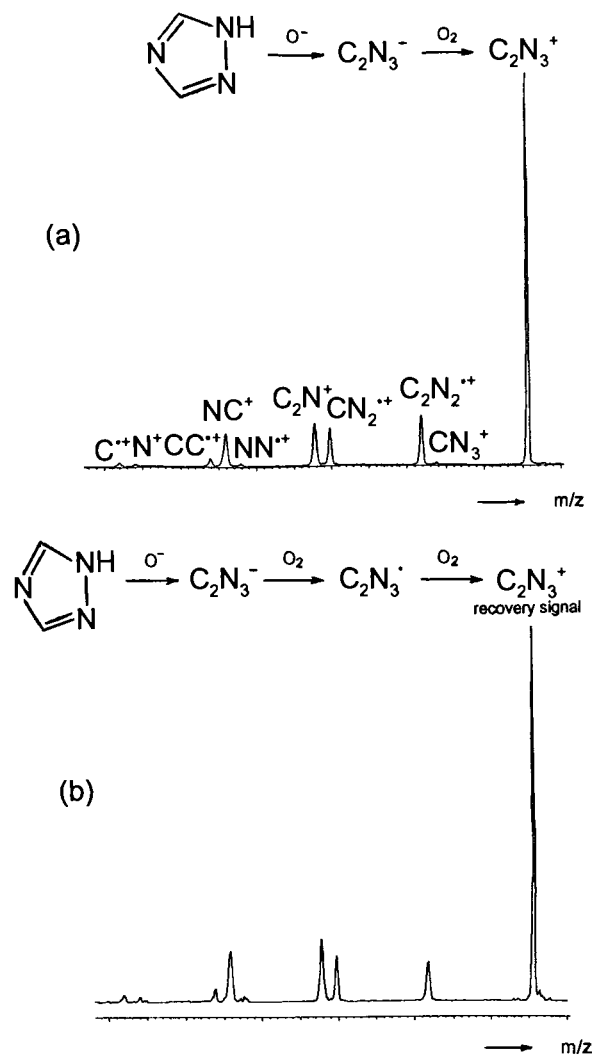


Figure 6. CR (a) and  $^- \text{NR}^+$  (b) mass spectra of  $\text{C}_2\text{N}_3^-$  ions generated by deprotonation of 1*H*-1,2,4-triazole

baric fragment ions of interest, unfortunately, precludes further CR/CA measurements.

The results here presented shed light on the existence of two distinguishable isomers of  $C_2N_3^-$  with the connectivities NNCCN and NCNCN in their anions, radicals and cations. These cumulenes constitute adequate precursors to tetra- and triatomic ions whose collisional-activation analysis further supports the structural assignment of the parent isomers and helps understand the mechanism of dinitrogen extrusion from them.

We thank the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for financial support.

## Experimental

All the reactions to generate  $C_2N_3^-$  are carried out in the chemical ionization (CI) source of the Berlin four-sector mass spectrometer of BEBE configuration<sup>[7]</sup>. Acetonitril (Merck) is injected into the CI source by a capillary jet, cyanoguanidine (Aldrich) and 1*H*-1,2,4-triazole (Aldrich) access the source by a mobile probe insert, heated within the range of 100–175 °C. The reagent gases enter through independent inlets. The total pressure in the source is ca.  $10^{-7}$  bar at a temperature of 200 °C.

For the CR experiments, the beam of  $m/z = 66$  anions, selected by *B*(1) and *E*(1), is forced to collide with  $O_2$  [80% transmittance (*T*)]. The ions of permuted charge, along with the fragments derived from them, are recorded by scanning *B*(2). The  $^-NR^+$  experiments consist of consecutive neutralization and reionization with  $O_2$  as target gas at 80% *T* in each step. Mass selection and scanning are analogous to the CR case. The CR/CA measurements proceed as the CR experiments but followed by selection of a fragment ion of interest (derived from  $m/z = 66$ ) with *B*(2), further

collision of it with He at 80% *T*, and final scanning with *E*(2). In all cases, signal-averaging techniques are controlled by an AMD Intectra data system.

- [1] <sup>[1a]</sup> C. A. Muedas, D. Sülzle, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes*, **1992**, *113*, R17. — <sup>[1b]</sup> D. Sülzle, P. E. O'Bannon, H. Schwarz, *Chem. Ber.* **1992**, *125*, 279. — <sup>[1c]</sup> D. Sülzle, K. Seemeyer, B. Witulski, H. Hopf, H. Schwarz, *Chem. Ber.* **1991**, *124*, 1481, and references therein. — <sup>[1d]</sup> D. Sülzle, K. Seemeyer, H. Schwarz, B. Witulski, H. Hopf, *Int. J. Mass Spectrom. Ion Processes* **1991**, *105*, R1.
- [2] S. R. Kass, J. Filley, J. M. Van Doren, C. H. DePuy, *J. Am. Chem. Soc.* **1986**, *108*, 2849.
- [3] <sup>[3a]</sup> M. M. Bursey, *Mass Spectrom. Rev.* **1990**, *9*, 555. — <sup>[3b]</sup> J. H. Bowie, *Mass Spectrom. Rev.* **1984**, *3*, 161. — <sup>[3c]</sup> K. Levsen, H. Schwarz, *Mass Spectrom. Rev.* **1983**, *2*, 77. — <sup>[3d]</sup> J. H. Beynon, *Proc. R. Soc. London, A* **1981**, *378*, 1. — <sup>[3e]</sup> R. G. Cooks (Ed.), *Collision Spectroscopy*, Plenum Press, New York, **1978**.
- [4] For most recent reviews on neutralization-reionization mass spectrometry (NRMS), see: <sup>[4a]</sup> F. W. McLafferty, *Adv. Mass Spectrom.*, in press. — <sup>[4b]</sup> F. W. McLafferty, *Science* **1990**, *247*, 925. — <sup>[4c]</sup> J. K. Terlouw, *Adv. Mass Spectrom.* **1989**, *11*, 984. — <sup>[4d]</sup> J. L. Holmes, *Mass Spectrom. Rev.* **1989**, *8*, 513. — <sup>[4e]</sup> H. Schwarz, *Pure Appl. Chem.* **1989**, *61*, 685.
- [5] F. M. Bickelhaupt, R. H. Fokkens, L. J. de Koning, N. M. M. Nibbering, E. J. Baerends, S. J. Goede, F. Bickelhaupt, *Int. J. Mass Spectrom. Ion Processes* **1991**, *103*, 157.
- [6] Preliminary CR/CA results on  $m/z = 38$  from CCNC<sup>-</sup>, generated by deprotonation of isocyanoacetylene, reveal a fragmentation pattern different from that reported in Figure 5: C. A. Muedas, D. Lenz, D. Sülzle, H. Schwarz, work in progress.
- [7] A detailed description of the machine can be found in: <sup>[7a]</sup> R. Srinivas, D. Sülzle, T. Weiske, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 369. — <sup>[7b]</sup> R. Srinivas, D. Sülzle, W. Koch, C. H. DePuy, H. Schwarz, *J. Am. Chem. Soc.* **1991**, *113*, 5970.

[147/92]

Heft 6 wurde am 2. Juni 1992 ausgegeben.

© VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1992 — Printed in the Federal Republic of Germany.

Verantwortlich für den Inhalt: Prof. Dr. Heinrich Nöth, München (Teil A), Prof. Dr. Henning Hopf, Braunschweig (Teil B). Redaktion: Dr. Robert Temme, Weinheim.

VCH Verlagsgesellschaft mbH (Geschäftsführer: Hans Dirk Köhler, Dr. Karlheinz Köpfer), Pappelallee 3, Postfach 101161, D-6940 Weinheim.

Anzeigenleitung: R. J. Roth, Weinheim.

Die Wiedergabe von Gebrauchsnamen, Handelsnamen, Warenbezeichnungen und dgl. in dieser Zeitschrift berechtigt nicht zu der Annahme, daß solche Namen ohne weiteres von jedermann benutzt werden dürfen. Vielmehr handelt es sich häufig um gesetzlich geschützte eingetragene Warenzeichen, auch wenn sie nicht als solche gekennzeichnet sind.

Alle Rechte, insbesondere die der Übersetzung in andere Sprachen, vorbehalten. Kein Teil dieser Zeitschrift darf ohne schriftliche Genehmigung des Verlages in irgendeiner Form — durch Photokopie, Mikrofilm oder irgendein anderes Verfahren — reproduziert oder in eine von Maschinen, insbesondere von Datenverarbeitungsanlagen verwendbare Sprache übertragen oder übersetzt werden. — All rights reserved (including those of translation into other languages). No part of this issue may be reproduced in any form — by photoprint, microfilm, or any other means — nor transmitted or translated into a machine language without the permission in writing of the publishers. — Von einzelnen Beiträgen oder Teilen von ihnen dürfen nur einzelne Vervielfältigungsstücke für den persönlichen oder sonstigen eigenen Gebrauch hergestellt werden. Die Weitergabe von Vervielfältigungen, gleichgültig zu welchem Zweck sie hergestellt werden, ist eine Urheberrechtsverletzung. — Der Inhalt dieses Heftes wurde sorgfältig erarbeitet. Dennoch übernehmen Autoren, Herausgeber, Redaktion und Verlag für die Richtigkeit von Angaben, Hinweisen und Ratschlägen sowie für eventuelle Druckfehler keine Haftung. — This journal was carefully produced in all its parts. Nevertheless, authors, editors and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

**Valid for users in the USA:** The appearance of the code at the bottom of the first page of an article in this journal (serial) indicates the copyright owner's consent that copies of the article may be made for personal or internal use, or for the personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay the stated percopy fee through the Copyright Clearance Center, Inc., for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to other kinds of copying, such as copying for general distribution, for advertising or promotional purposes, for creating new collective work, or for resale. For copying from back volumes of this journal see »Permissions to Photo-Copy: Publisher's Fee List« of the CCC.

In der Zeitschrift werden keine Rezensionen veröffentlicht; zur Besprechung eingehende Bücher werden nicht zurückgesandt.

Satz und Druck: Krebs-Gehlen Druckerei, Hemsbach/Bergstraße.

Printed on acid-free and low-chlorine paper / Gedruckt auf säurefreiem und chlorarm gebleichtem Papier