Deformation Density of a *cis,cis*-Trialkyltriaziridine

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We determined the deformation densities of 6,8,9-triacetoxy-2,3,4-triazatetracyclo[$3.3.1.0^{2,4}.0^{3,7}$]nonane (1), a triaziridine derivative, from low temperature X-ray data (105 K). Significant electron density peaks of the strongly bent N−N bonds of the triaziridine ring could not be found by the X−X method. The density maxima of the lone pairs of the nitrogen atoms and of the C−C, C−N and C-O bonds appear clearly.

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Auf der Basis von Tieftemperatur-Röntgenbeugungsdaten (105 K) haben wir die Deformationsdichte von 6,8,9-Triacetoxy-2,3,4-triazatetracyclo[$3.3.1.0^{2,4}.0^{3,7}$]nonan (1) bestimmt. Mit der X−X-Methode konnten keine signifikanten Elektronendichtemaxima auf den stark gebogenen N−N-Bindungen gefunden werden. Die Dichtemaxima an den einsamen Elektronenpaaren der Stickstoffatome und in den C−C-, C−N- und C−O-Bindungen traten klar hervor.

Through photolysis (thermolysis) of specifically designed azo/azide substrates unusually stable, rigid *cis,cis*-trialkyltriaziridines have been prepared[1]. PE analysis revealed a strong interaction between the three *syn*-oriented nitrogen lone pairs and a marked influence of the substitution upon the energy of the respective highest molecular orbitals[2]. Triaziridine 1 (6,8,9-trisacetoxy-2,3,4-triazatetracyclo-[$3.3.1.0^{2,4}.0^{3,7}$]nonane) the structure of which had been determined[2] was now chosen for deformation density measurements, from which better insight into the electron density in the N_3 ring was expected. Therefore, we carried out low-temperature X-ray measurements at 105 K and determined the deformation densities by the X−X method[3]. From such investigations, bent bonds were established for cyclopropane, aziridine, and oxirane rings[4]. For the triaziridine ring, experimental results about the density distribution do not exist.

R = O−C(=O)−CH₃

1
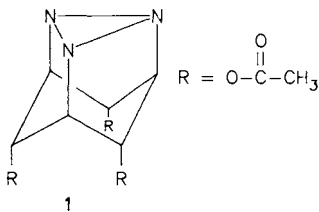
The N−N distance of 1.499(5) Å [averaged; Figure 1; at room temperature: 1.502(5) Å[2]] is comparatively[2] long because of repulsive interactions between the lone pairs of the nitrogen atoms and the substituents. The other bond distances, particularly on the periphery of the molecule are 0.01 Å longer on the average compared with the room temperature data[2]. This effect, generally found with low-temperature measurements, arises from reduction of the thermal motion of the atoms and consequently the vibration effects. Furthermore, the atomic coordinates of the low-temperature

structure are refined only with the high-order reflections (see Experimental) which eliminates the disturbing influence of the bonding electrons. Slight deviations of the atomic positions reflect the higher precision obtained with low-temperature data.

The sections through the triaziridine ring plane and thus through the N−N bonds do not show significant electron density contributions (Figure 2). Proceeding from the negative density regions at the atomic positions ($-0.1 e/Å^3$ on the average), the electron density rises only to humps of $0-0.5$ e/Å^3, which are shifted outwards by 0.5 Å on the average from the N−N bond axes. The missing of electron density maxima in the N−N bonds are not surprising, since for C−N[5], N−N[6], C−O[7], N−O[8], and C−F[9] bonds only small deformation densities have been detected − decreasing in the order C−N > C−O > N−N > O−O[10]. In the O−O bonds actually no deformation density was found[10,11]. The lowering of the electron density in the N−N bonds of 1 beyond the limit of significance can be explained by the weakening of these bonds. They are strongly bent and stretched by repulsive interactions along these bonds, which results in comparatively long bond distances. According to recent studies, the electron densities in bonds with heteroatoms generally appear too low, because spherical atoms rather than valence-state atoms are substracted from the total density to form the deformation density[12]. The maxima of the lone pairs at the nitrogen atoms, however, can clearly be recognized (Figure 3). They lie above the ring plane of the triaziridine by 0.5 Å and have an average distance of 2.1 Å from each other.

The density maxima of all C−C bonds of the cyclohexane ring of 1 are regularly shaped (Figure 4). They can be taken as internal standards for the quality of this deformation density study. As expected, the density peaks of the C=O
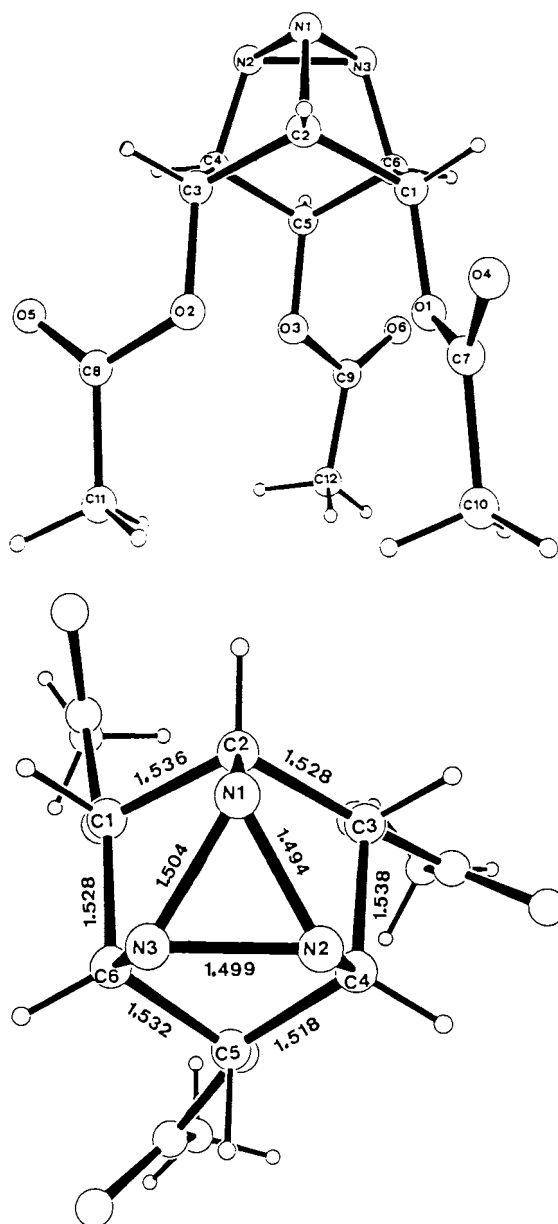
Figure 1. Structure and selected bond lengths [Å] of 1. The standard deviations are 0.002 Å. Selected bond angles (averaged; except for acetoxy groups) with scatter [°]: N—N—N 60.0(3), N—C—C 101.8(5), C—C(N)—C 114.0(8), C—C(O)—C 101.2(3); standard deviations 0.001°.
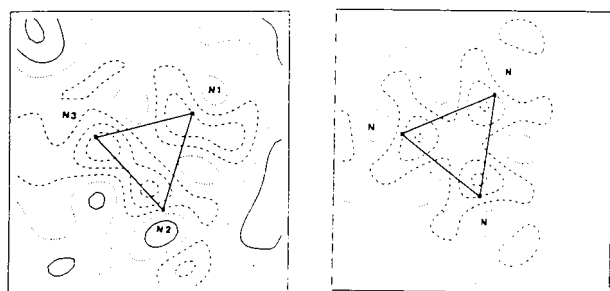

Figure 2. Deformation densities in the section through the plane of the triaziridine ring (left). In the right section the electron densities of chemically equivalent N—N bonds are averaged (C_3 symmetry). The contour intervals are 0.05 e/Å³. The zero line is dotted, negative regions have dashed lines.
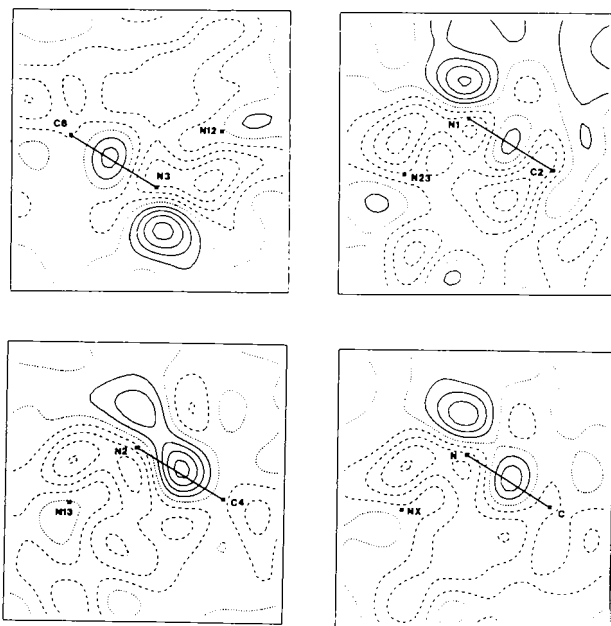

Figure 3. Deformation density sections through the planes N12, N3, C6; N23, N1, C2 and N13, N2, C4 (N12 is the center of N1 — N2; accordingly N13 and N23). 4th section average.
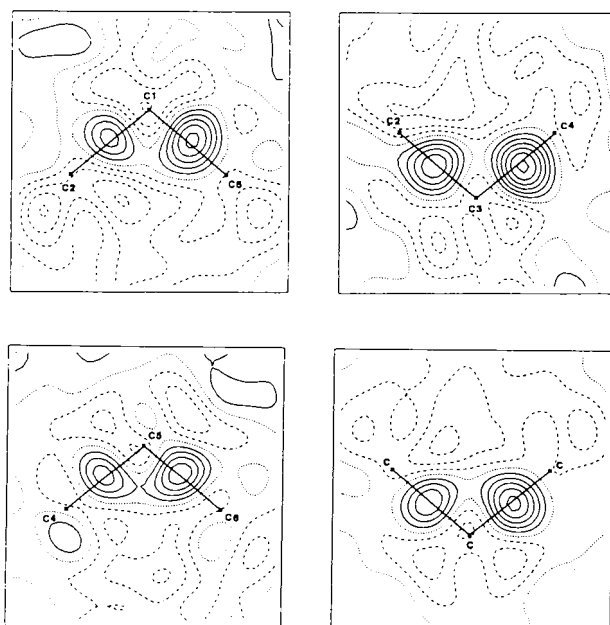

Figure 4. Deformation density section through the atoms of the six-membered ring. Section through the planes C1, C2, C6; C2, C3, C4 and C4, C5, C6 and averaged section.

double bonds of the ester groups are higher than the maxima of the C—O single bonds (Figure 5). The latter ones have the same order of magnitude as the electron density maxima of the C—N bonds (Figure 3). Because of the greater flexibility of the acetyl groups, the electron density of the lone pairs of the oxygen atoms is smeared extensively. The standard deviations[13] of the deformation densities in the regions discussed are 0.055 e/Å³.

Table 1. Refinement procedures (full matrix, F^2) of **1**

sin Θ/λ range	reflec-tions	unobs. $\geq 2.5\sigma(I)$	unobs. refin.[a]	obs.	total refin.[a]	vari-ables	ratio refl./variab.	R factor (%)
0.0−0.65	3144	1026	470	2118	2583	250	10.3	3.26
0.0−0.70	3695	1242	648	2453	3096	250	12.4	3.30
0.60−1.15	4473	2630	2046	1843	3888	190	20.5	3.68
0.70−1.15	3233	2058	1664	1175	2839	190	14.9	4.45

[a] Included in the refinement.
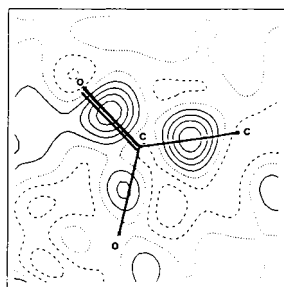
Figure 5. Averaged deformation density of the three ester groups.

Experimental

The low-temperature data were collected with a crystal of **1** of the size $0.4 \times 0.35 \times 0.25$ mm enclosed in a Mark capillary at a temperature of 105 ± 1 K with an automatic diffractometer with low-temperature equipment (Enraf-Nonius CAD4, Mo-K_α radiation, graphite monochromator, $\omega - 2\Theta$ scan). To prevent icing, the diffractometer was covered with a plastic tent. From 125 high-order reflections, the cell dimensions have been determined: $a = 8.270(1)$, $b = 12.520(2)$, $c = 13.332(2)$ Å; $\beta = 97.60(1)$; $D_{calc} = 1.45$ Mg/m^3; monoclinic space group $P2_1/n$, $Z = 4$; $\mu = 110$ m^{-1}.

With the first set of intensities up to $\Theta = 28°$ the structural model from room temperature measurements[2] was refined. The reflections that had to be expected as observed ($F_{calc} \geq 3.0$) in the range of $28°$ to $55°$ in Θ were selected by computation and subsequently measured. The independent data set ($\Theta = 2°-55°$) was collected three times, with a total of 21946 reflections. Polarisation, Lorentz, and absorption (numerical[14]) corrections were applied. After averaging, an independent data set of 6928 reflections was obtained, 3628 of which were classified as observed [$I \geq 2.5 \, \sigma(I)$]. The R factor of the averaging (R_{int}) is 0.034. The refinement of the structure (non hydrogen atoms anisotropic, hydrogen atoms isotropic) and the calculation of the deformation density was carried out according to the following scheme:

i) Refinement of all atoms and of the scale factor with reflections in the range of $\sin\Theta/\lambda < 0.70$ Å^{-1}.

ii) Refinement of the non hydrogen atoms and of the scale factor with the reflections of the Bragg angle range $0.60 < \sin\Theta/\lambda < 1.15$ Å^{-1}. The hydrogen atoms have been taken unchanged from i).

iii) Refinement of the scale factor alone with the reflections from $\sin\Theta/\lambda = 0-1.15$ Å^{-1}.

iv) Calculation of the structure factors (F_{calc}) of the range $\sin\Theta/\lambda = 0-0.60$ Å^{-1} with the structure model of the high-order refinement ii) and scaling of the observed structure factors (F_{obs}) in the same range with the scale factor of iii).

Table 2. Atomic coordinates ($\times 10^4$) of the non hydrogen atoms with their standard deviations and the averaged anisotropic displacement parameters ($U_{eq} \times 10^4$ Å^2)

Atom	x	y	z	$U_{eq} \times 10^4 [\text{Å}^2]$
O1	1963(1)	1308(1)	6164(1)	181(2)
O2	3256(1)	3308(1)	5850(1)	189(2)
O3	4331(1)	2291(1)	7664(1)	193(2)
O4	203(2)	1243(2)	4725(1)	306(4)
O5	4833(2)	4745(1)	6289(2)	309(3)
O6	4560(2)	1105(1)	8946(1)	258(3)
N1	-443(2)	3509(1)	7053(1)	220(3)
N2	776(2)	3959(1)	7871(1)	227(3)
N3	67(2)	2874(1)	8000(1)	210(3)
C1	778(1)	1915(1)	6610(1)	168(2)
C2	490(2)	3075(1)	6258(1)	183(3)
C3	2034(2)	3759(1)	6392(1)	186(3)
C4	2427(2)	3783(1)	7552(1)	192(3)
C5	2890(2)	2699(1)	8013(1)	179(2)
C6	1300(2)	2074(1)	7743(1)	180(3)
C7	1525(2)	1032(1)	5187(1)	207(3)
C8	4651(2)	3876(1)	5889(1)	212(3)
C9	5099(2)	1498(1)	8228(1)	199(3)
C10	2874(3)	453(2)	4773(2)	308(4)
C11	5910(2)	3281(2)	5404(1)	261(3)
C12	6659(2)	1193(2)	7848(2)	294(3)

From the structure factors F_{obs} and F_{calc} of iv) the deformation densities were calculated. The numbers of reflections and variables included are listed in Table 1. The atomic coordinates of the hydrogen atoms and the equivalent isotropic displacement factors (U_{eq}) from the high-order refinement ii) are given in Table 2. According to the Hirshfeld test[15], the difference of the thermal vibration contribution of two atoms along the bond connecting both atoms should be smaller than 0.001 Å^2. Only for a few atoms, particularly of the ester groups, this limit was exceeded. The average value is 0.0006 Å^2. Further details of measuring and refinement procedures have already been described[16]. The coordinates of the hydrogen atoms and their isotropic displacement factors, the bond lengths and angles, the structure factor tables and further details of the structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-53213, the names of the authors, and the journal citation.

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