Electron density distribution in crystal of polyfluorinated tetraazapentalene based on X-ray diffraction data at 130 K

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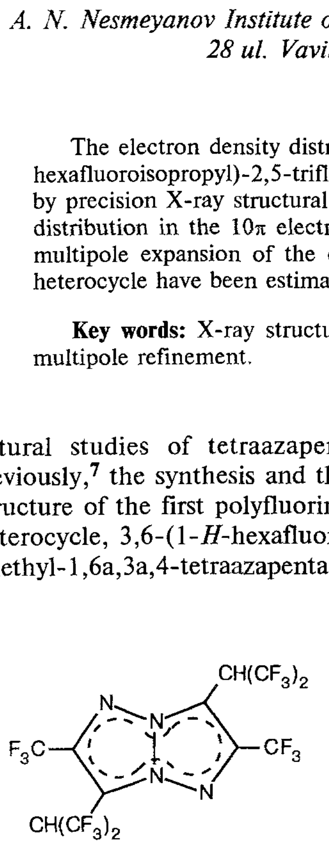
The electron density distribution in crystal of a new heterocyclic compound, 3,6-(1-*H*-hexafluoroisopropyl)-2,5-trifluoromethyl-1,6a,3a,4-tetraazapentalene, has been determined by precision X-ray structural analysis at 130 K. The character and features of the electron distribution in the 10π electron system of the heterocycle have been established using the multipole expansion of the electron density. The charges on the C and N atoms of the heterocycle have been estimated based on X-ray diffraction data.

Key words: X-ray structural analysis, tetraazapentalenes, electron density distribution, multipole refinement.

The structural studies of tetraazapentalenes are scarce.[1–6] Previously,[7] the synthesis and the molecular and crystal structure of the first polyfluorinated derivative of this heterocycle, 3,6-(1-*H*-hexafluoroisopropyl)-2,5-trifluoromethyl-1,6a,3a,4-tetraazapentalene (**1**) were reported.



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In an effort to elucidate the character and features of the electron density distribution in the aromatic 10π electron system of the tetraazapentalene moiety, we performed the precision X-ray diffraction study of a crystal of **1** at 130 K. The multipole model proposed by Hansen and Coppens[8] allows the asphericity of the charge distribution resulting from chemical bonding to be taken into account in the analytical form and the numerical characteristics of this distribution to be refined; this model was used in the analysis of the electron distribution, making it possible to compare these characteristics with the results of quantum-chemical calculations of tetraazapentalenes.[9]

In the multipole model under consideration, the aspherical electron density of each atom $\rho_{\text{atom}}(r)$ is represented as the sum of the nondeformed (spherical) Hartree-Fock densities of electrons of the core (ρ_{core}) and the valence shells (ρ_{val}), as well as the spherical harmonics Y_{lm} describing the deformation of the valence shell when the atom is involved in a chemical bond. Therefore:

$$\rho_{\text{atom}}(r) = P_c\rho_{\text{core}}(r) + P_{\text{val}}k'^3\rho_{\text{val}}(k'r) + \\ + \sum_{l=0}^{4} k''^3 R_l(k''r) \sum_{m=-l}^{l} P_{lm} Y_{lm}(|r|/r),$$

where P_c, P_{val}, and P_{lm} are refined population coefficients, the parameter k' describes the expansion (contraction) of a valence shell, $R_l(r)$ is a radial Slater-type function, and k'' is the exponent of the radial function. Spherical harmonics are normalized so that $P_{lm} = 1$ corresponds to the transfer of one electron from the negative to the positive lobe of the deformation function. The scheme for choosing the parameters of radial functions was reported in Ref. 8.

Experimental

An approximately isometric single crystal with linear dimensions of ~0.3 mm was chosen for precision X-ray diffraction analysis. The diffraction experiment was carried out on an automated four-circle Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scan technique, 2θ ≤ 90°) at 130±1 K.

Crystals of **1** are monoclinic, at 130 K: a = 5.709(1), b = 10.978(2), c = 13.388(3) Å, β = 96.35(2), V = 833.9(6) Å^3, the space group is $P2_1/c$, Z = 2; molecules **1** are located on crystallographic inversion centers. Of the total of 7707 measured reflections (in the near region of 2θ ≤ 40°, reflections were collected within a full sphere; in the range 40° ≤ 2θ ≤ 90°, reflections were collected within a hemisphere in reciprocal space), 2659 independent observed reflections with $I \geq 4\sigma$ were

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used in subsequent calculations and refinement. The internal merging R factor for intensities of equivalent reflections R_{int} is 0.032 (for reflections in the "near region", R_{int} = 0.021). When refining the parameters of the structure, we used the data from Ref. 7 as a model. The structure was refined by the full-matrix least-squares method with anisotropic (for nonhydrogen atoms) and isotropic (for the H atom) thermal parameters. No correction for absorption was applied because absorption is insignificant; the correction for isotropic secondary extinction was also negligible. At the final stage of refinement, we used the quasi-high-order refinement scheme[10] with weights $f = 1-\exp[-B(\sin\theta/\lambda)^2]$ (B = 5.0 Å^2) for calculating deformation electron density maps with the aim of obtaining the proper values of the positional and thermal parameters for nonhydrogen atoms. The results of this refinement are as follows: R = 0.031, R_w = 0.032, and GOF = 1.88. Atomic coordinates and temperature factors are given in Tables 1 and 2; the bond lengths and bond angles are presented in Table 3. The overall view of molecule **1** and atomic numbering scheme are shown in Fig. 1.

Table 1. Atomic coordinates ($\times 10^4$; $\times 10^3$ for H atoms) and equivalent isotropic temperature factors (Å$\times 10^3$)

Atom	x	y	z	U
F(1)	4836(1)	−1035(1)	7500(1)	30(1)
F(2)	6814(1)	−54(1)	6489(1)	25(1)
F(3)	4732(1)	931(1)	7453(1)	27(1)
F(4)	75(1)	2399(1)	2635(1)	27(1)
F(5)	2344(1)	2713(1)	4003(1)	23(1)
F(6)	20(1)	4140(1)	3378(1)	26(1)
F(7)	10(1)	3464(1)	5596(1)	25(1)
F(8)	−3083(1)	4281(1)	4809(1)	30(1)
F(9)	−3385(2)	2626(1)	5653(1)	31(1)
N(1)	1896(1)	963(1)	5701(1)	13(1)
N(2)	152(1)	616(1)	5019(1)	11(1)
C(1)	2701(1)	−111(1)	6100(1)	12(1)
C(2)	−1507(1)	1124(1)	4318(1)	12(1)
C(3)	−1772(2)	2459(1)	4115(1)	13(1)
C(4)	4772(2)	−69(1)	6898(1)	15(1)
C(5)	−2040(2)	3222(1)	5060(1)	18(1)
C(6)	199(2)	2941(1)	3528(1)	16(1)
H	−315(1)	258(1)	368(2)	18(3)

Table 2. Anisotropic thermal parameters (Å$\times 10^3$) in the form of $T = \exp[-2\pi(h^2a^{\star 2}U_{11} + k^2b^{\star 2}U_{22} + ... + 2hka^{\star}b^{\star}U_{12})]$ for nonhydrogen atoms in the structure of **1**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(1)	32(1)	32(1)	24(1)	14(1)	−12(1)	−9(1)
F(2)	12(1)	39(1)	22(1)	−4(1)	2(1)	2(1)
F(3)	22(1)	32(1)	26(1)	−17(1)	−8(1)	6(1)
F(4)	34(1)	33(1)	16(1)	−2(1)	8(1)	−6(1)
F(5)	13(1)	29(1)	27(1)	7(1)	2(1)	0(1)
F(6)	27(1)	16(1)	35(1)	9(1)	5(1)	−1(1)
F(7)	28(1)	23(1)	23(1)	−8(1)	−4(1)	0(1)
F(8)	34(1)	18(1)	36(1)	−3(1)	3(1)	12(1)
F(9)	40(1)	28(1)	29(1)	−5(1)	21(1)	−6(1)
N(1)	13(1)	14(1)	13(1)	−1(1)	−2(1)	−1(1)
N(2)	12(1)	11(1)	11(1)	−1(1)	−0(1)	−0(1)
C(1)	12(1)	14(1)	12(1)	−1(1)	−0(1)	−0(1)
C(2)	12(1)	12(1)	12(1)	0(1)	−1(1)	1(1)
C(3)	13(1)	12(1)	14(1)	1(1)	0(1)	1(1)
C(4)	13(1)	18(1)	13(1)	−1(1)	−1(1)	0(1)
C(5)	20(1)	14(1)	20(1)	−2(1)	4(1)	2(1)
C(6)	17(1)	15(1)	16(1)	3(1)	1(1)	0(1)

Multipole parameters, including hexadecapole terms, were refined only for the atoms of the heterocycle; the remaining parameters for the atoms of the structure were fixed. The refinement was performed using 1280 reflections with $\sin\theta/\lambda \le 0.60$ Å^{-1}; local m symmetry was assumed for each atom of the heterocycle. The local coordinate systems used in this refinement are shown in Fig. 2. The results of the multipole refinement are as follows: R = 0.024, R_w = 0.032, and GOF = 1.62. The corresponding multipole population coefficients for atoms of the heterocycle are given in Table 4. All calculations were performed on an IBM PC/AT computer using the SHELXTL PLUS program package.[11] The multipole refinement was carried out using the MOLLY program,[8] adapted to a personal computer.

Results and Discussion

The geometric parameters of molecule **1** in the crystal are virtually identical with those observed previously for this compound at 183 K.[7] There is only a slight elongation of the C—F bond at the lower temperature (the average value is 1.333(1) Å as opposed to

Table 3. The bond lengths (d/ Å) and bond angles (ω/deg) in the structure of **1**

Bond	d	Bond	d
F(1)—C(4)	1.330(1)	N(1)—C(1)	1.354(1)
F(2)—C(4)	1.341(1)	N(2)—C(2)	1.376(1)
F(3)—C(4)	1.328(1)	N(2)—N(2′)*	1.365(1)
F(4)—C(6)	1.330(1)	C(1)—C(4)	1.504(1)
F(5)—C(6)	1.339(1)	C(1)—C(2′)	1.389(1)
F(6)—C(6)	1.335(1)	C(2)—C(3)	1.496(1)
F(7)—C(5)	1.330(1)	C(2)—C(1′)	1.389(1)
F(8)—C(5)	1.333(1)	C(3)—C(5)	1.539(1)
F(9)—C(5)	1.335(1)	C(3)—C(6)	1.536(1)
N(1)—N(2)	1.329(1)		
Angle	**ω**	**Angle**	**ω**
N(2)—N(1)—C(1)	102.5(1)	F(1)—C(4)—C(1)	111.9(1)
N(1)—N(2)—C(2)	139.4(1)	F(2)—C(4)—C(1)	111.2(1)
N(1)—N(2)—N(2′)	113.1(1)	F(3)—C(4)—C(1)	111.2(1)
C(2)—N(2)—N(2′)	107.5(1)	F(7)—C(5)—F(8)	107.7(1)
N(1)—C(1)—C(4)	117.4(1)	F(7)—C(5)—F(9)	107.9(1)
N(1)—C(1)—C(2′)	114.1(1)	F(8)—C(5)—F(9)	107.9(1)
C(4)—C(1)—C(2′)	128.5(1)	F(7)—C(5)—C(3)	113.0(1)
N(2)—C(2)—C(3)	124.7(1)	F(8)—C(5)—C(3)	110.5(1)
N(2)—C(2)—C(1′)	102.8(1)	F(9)—C(5)—C(3)	109.8(1)
C(3)—C(2)—C(1′)	132.5(1)	F(4)—C(6)—F(5)	107.3(1)
C(2)—C(3)—C(5)	113.7(1)	F(4)—C(6)—F(6)	108.0(1)
C(2)—C(3)—C(6)	111.4(1)	F(5)—C(6)—F(6)	107.8(1)
C(5)—C(3)—C(6)	112.2(1)	F(4)—C(6)—C(3)	109.7(1)
F(1)—C(4)—F(2)	106.9(1)	F(5)—C(6)—C(3)	112.1(1)
F(1)—C(4)—F(3)	108.7(1)	F(6)—C(6)—C(3)	111.6(1)
F(2)—C(4)—F(3)	106.7(1)		

* The N(2′) atom is related to the N(2) atom by the inversion center ($-x,-y,1-z$).

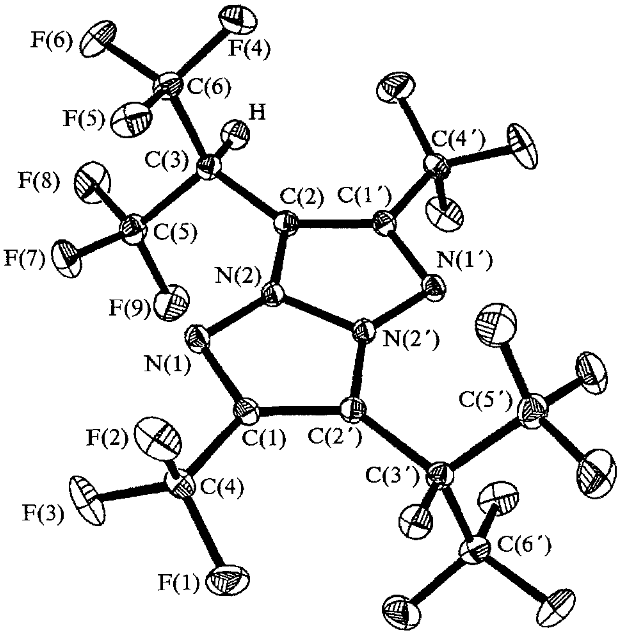


Fig. 1. The overall view of molecule **1**, atoms are represented by thermal ellipsoids (p = 50%).

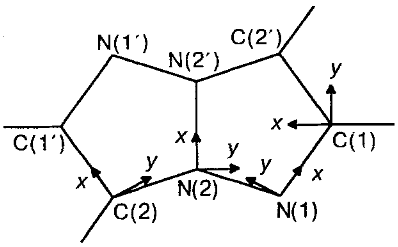


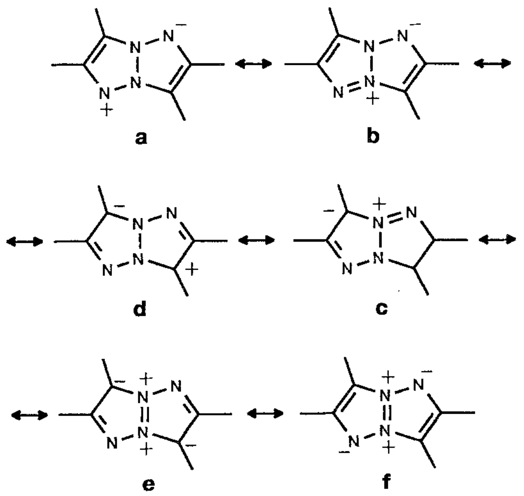
Fig. 2. Local coordinate systems used in the multipole refinement of the structure of **1**.

1.329(2) Å),[7] which is, apparently, caused by a decrease in the librational amplitudes for CF_3 groups. The central heterocycle of **1** is planar; the deviations of the C(3) and C(4) atoms from the mean plane of the cycle (planar within 0.001 Å) are 0.007 and 0.037 Å. The HC(3)C(2)N(2) and F(1)C(4)C(1)N(1) torsion angles are 171 and 155°, respectively, *i.e.*, the H and F(1) atoms lie virtually in the plane of the heterocycle. The substantial distortion of the exocyclic bond angles compared to the ideal value of 120° at the planar-trigonal C(1), C(2), and N(2) atoms should be mentioned. In particular, the N(1)N(2)C(2), C(3)C(2)C(1′) and C(4)C(1)C(2′) bond angles increase to 139.4(1)°, 132.5(1)°, and 128.5(1)°, respectively. The substantial enlargement of the two latter angles is caused, apparently, by steric interactions, whereas the enlargement of the N(1)N(2)C(2) angle stems from the formation of the bicyclic system.

The bond lengths in the heterocycle have values typical of C—C, N—N, and C—N bonds with an order of 1.5, which reflects the presence of substantial electron delocalization in the aromatic 10π electron tetraazapentalene system of **1**. However, based only on the analysis of geometric characteristics of **1**, it is impossible to determine with certainty, which one of the following canonical ionic structures makes the major contribution to the electronic structure of the molecule:

Table 4. Multipole population coefficients P_{lm} for atoms of the heterocycle in the structure of **1** ($\times 10^2$)

P_{lm}	C(1)	C(2)	N(1)	N(2)
P_{val}	9(4)	4(2)	−19(3)	21(4)
P_{11+}	18(2)	15(3)	16(3)	−17(2)
P_{11-}	15(4)	8(2)	−12(3)	21(3)
P_{20}	−25(3)	−19(2)	6(2)	10(2)
P_{22+}	−14(2)	6(2)	−9(2)	22(4)
P_{22-}	9(2)	−11(2)	5(2)	9(3)
P_{31+}	12(3)	16(4)	8(2)	−15(2)
P_{31-}	2(3)	−9(1)	0(4)	−4(1)
P_{33+}	36(4)	47(6)	9(2)	4(2)
P_{33-}	9(3)	27(3)	35(3)	20(2)
P_{40}	5(4)	−9(2)	−12(6)	−16(2)
P_{42+}	2(3)	−8(3)	4(5)	10(2)
P_{42-}	−15(3)	14(2)	9(3)	6(2)
P_{44+}	9(4)	10(3)	6(2)	−11(4)
P_{44-}	−13(7)	9(2)	11(5)	19(5)



The quantum-chemical calculations of the optimized geometry of unsubstituted tetraazapentalene and its dinitro derivative (the 3-21G basis set) also reproduce incompletely the distribution of bond lengths in the heterocycle:[9] according to the results of the calculations, the length of the central N(2)—N(2′) bond is underestimated by 0.010—0.015 Å compared to the experimental value in **1**, while the N(1)—N(2) bond length, on the contrary, is overestimated by 0.035—0.042 Å.

Analysis of the deformation electron density maps and the results of the multipole refinement of the structure make it possible to obtain additional information on the characteristic features of electron delocalization in

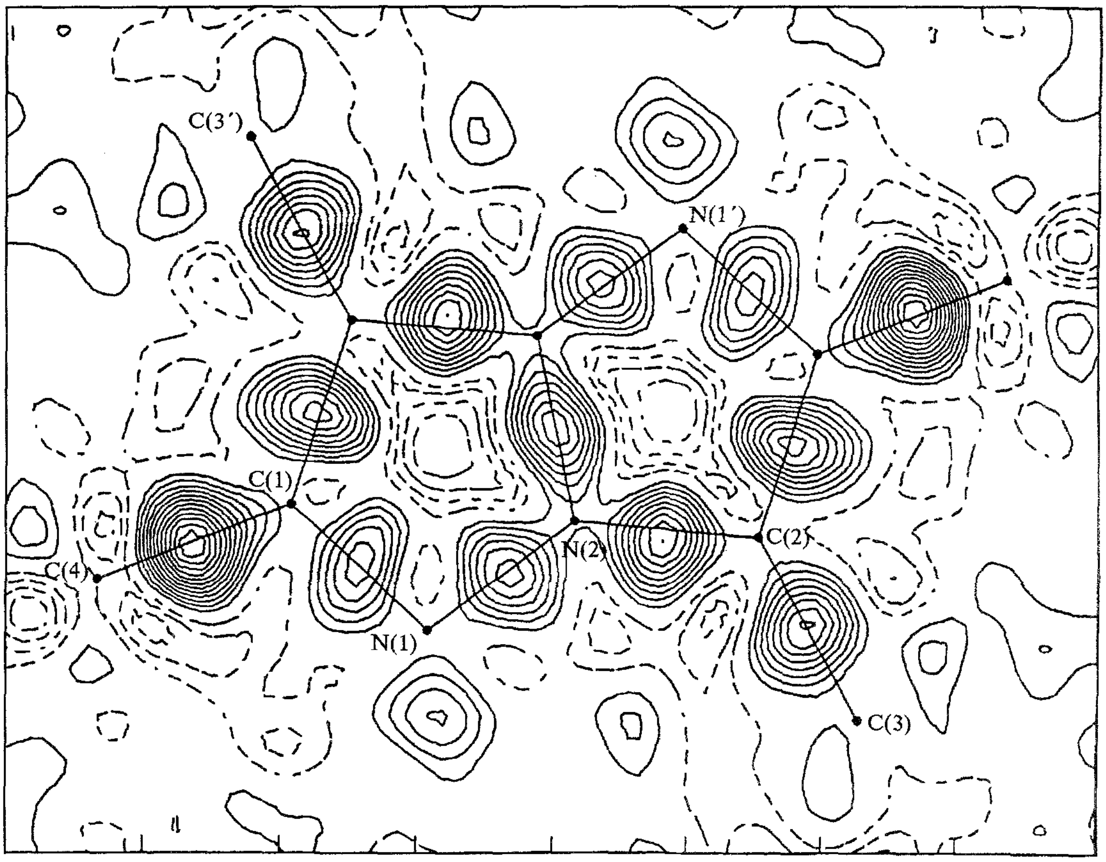
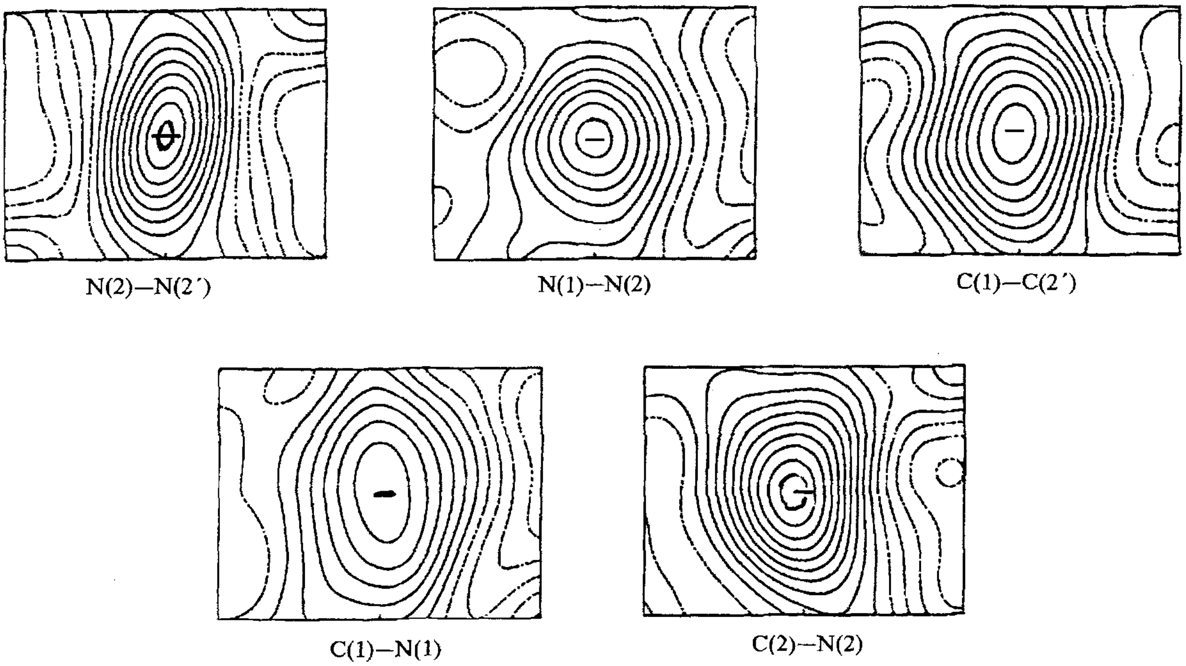


Fig. 3. Sections of the deformation electron density in the plane of the heterocycle of **1**. Contour intervals are 0.05 e/ Å^3, negative contours are denoted by dashed lines.

the studied heterocycle. The deformation electron density maps were calculated by the X—X method using small-angle reflections with $\sin\theta/\lambda \le 0.70$ Å^{-1}. The results of the quasi-high-order refinement were used as a model of the promolecule.

The section of the deformation electron density in the plane of the heterocycle is shown in Fig. 3. This section shows clearly the maxima of the deformation electron density located in the centers of all of the chemical bonds and the peaks near the N(1) and N(1′) atoms at a distance of 0.6 Å from the atomic nuclei and with the height of 0.25 e/ Å^3, thus completing the symmetry of the electron distribution around these atoms to planar-trigonal. Apparently, the maxima under consideration correspond to the lone electron pairs of the N(1) and N(1′) atoms with sp^2 hybridization. Figure 4 shows the sections of the deformation electron density passing through the centers of the bonds of the heterocycle and perpendicular to the plane of the heterocycle. These sections make it possible to identify the presence of π components in the bonds under consideration, which makes them helpful in elucidating the character of electron delocalization in π systems. As seen from this figure, all of the bonds in the heterocycle of **1**, except the N(1)—N(2) bond, are characterized by the elongated (ellipsoid) shape of the section of the deformation electron density along the direction normal to the plane of the cycle, *i.e.*, the presence of a substantial π component. It is remarkable that the sections of the deformation density of the central N(2)—N(2′) bond as well as of the C(1)—C(2′) bond are characterized by the largest ellipticity. Evidently, this is indicative of a larger degree of double bonding between the corresponding atoms. By contrast, the section of the deformation electron density through the N(1)—N(2) bond is almost circular, *i.e.*, the π component for this bond is, apparently, the smallest. Nevertheless, it should be pointed out that the N(1)—N(2) bond (1.329(1) Å) is substantially shorter than the central N(2)—N(2′) bond (1.365(2) Å), *i.e.*, according to the geometric characteristics of molecule **1**, the degree of double bonding between the N(1) and N(2) atoms should be substantially larger. This result demonstrates that the correlations between bond lengths and bond orders available in the literature should be considered with caution, at least for heterocyclic molecules, because the dependence of the molecular geometry (bond lengths) on different effects is apparently more complex than expected.

The features of the deformation electron density maps found in this work are supported by the results of



N(2)—N(2′) N(1)—N(2) C(1)—C(2′)

C(1)—N(1) C(2)—N(2)

Fig. 4. Sections of the deformation electron density through the centers of the C—C, C—N, and N—N bonds in the plane perpendicular to the plane of the heterocycle and the bond line. Contour intervals are 0.05 e/Å^3.

the multipole refinement of the structure of **1** (see Table 4). In particular, the significant values of the population coefficients P_{33+} and P_{33-} for the N(1), C(1), and C(2) atoms corresponding to multipole terms of trigonal symmetry with positive (P_{33+}) or negative (P_{33-}) lobes along bonds or along angle bisectors between bonds are indicative of sp^2 hybridization of these atoms. The terms P_{22+} and P_{22-}, which also cause π bonding, are significant for all atoms of the heterocycle. For the C(1), C(2), and N(2) atoms, the values of the coefficients P_{20} and P_{31+}, which cause π bonding, are significant, which demonstrates that the electron density concentrates above and below the plane of the ring. The smallest values of these terms (P_{20} = 0.06(2) and P_{31+} = 0.08(2)) are found for the N(1) atom, which is in agreement with the absence of a substantial π component for the N(1)—N(2) bond observed in the deformation electron density map (Fig. 4).

Hence, the shapes of sections of the deformation electron density and the analysis of the results of the multipole refinement suggest that the canonical ionic structure *f*, with a charge partition between the nitrogen atoms, a formally single N(1)—N(2) bond, and a formally double N(2)—N(2′) bond, apparently makes a major contribution to the electronic structure of the heterocycle of **1**. The atomic charges obtained from the X-ray diffraction data, (C(1) = −0.09(4), N(1) = −0.19(3), C(2) = +0.04(2), and N(2) = +0.21(4)), confirm this conclusion.

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