Chem. Ber. **118**, 2118 – 2126 (1985)

The Molecular and Electronic Structure of Dipiperidinosquaraine

Peter H. M. Budzelaar [a], *Hans Dietrich* [b], *Jürgen Macheleid* [a], *Robert Weiss* [a], and *Paul von Ragué Schleyer* * [a]

Institut für Organische Chemie der Universität Erlangen-Nürnberg[a],
Henkestr. 42, D-8520 Erlangen, and

Fritz-Haber-Institut der Max-Planck-Gesellschaft[b],
Faradayweg 4 – 6, D-1000 Berlin 33

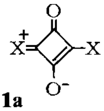
Received May 25, 1984

Dipiperidinosquaraine (**9**) crystallizes in the orthorhombic system, space group *Pnab*, with four molecules in a cell of dimensions a = 7.1798(9), b = 9.5362(8), and c = 18.788(2) Å. The molecule is located over a center of symmetry, so the four-membered ring (C – C = 1.456(1) Å av) is exactly planar; the nitrogen and oxygen atoms are nearly coplanar with the ring, with C – O = 1.2396(7) and C – N = 1.3112(7) Å. Both experimental and theoretical evidence indicates the presence of considerable C – N and C – O π-bonding, but only a small amount of C – C π-bonding in the squaraine system. The calculations indicate the presence of strong 1,3-repulsive interactions within the four-membered ring. Ring puckering, which is a common mechanism to alleviate these repulsions, is prevented here by the extensive C – N π-bonding.

Molekulare und elektronische Struktur von Dipiperidinoquadratain

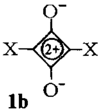
Dipiperidinoquadratain (**9**) kristallisiert im orthorhombischen Gitter, Raumgruppe *Pnab*, mit 4 Molekülen in einer Elementarzelle mit den Abmessungen a = 7.1798(9), b = 9.5362(8) und c = 18.788(2) Å. Das Molekül liegt auf einem Symmetriezentrum, d. h. der Vierring (C – C = 1.456(1) Å) ist genau planar; die Stickstoff- und Sauerstoffatome sind fast mit dem Ring coplanar, mit C – O = 1.2396(7) und C – N = 1.3112(7) Å. Sowohl die experimentellen als auch die theoretischen Daten zeigen beachtliche C – N- und C – O-π-Bindungen, aber nur eine geringfügige C – C-π-Bindung im Quadratainsystem. Die Berechnungen ergeben starke 1,3-abstoßende Wechselwirkungen im Vierring. Ringfaltung, ein sonst üblicher Mechanismus bei der Vermeidung solcher Abstoßungen, wird hier durch die starke C – N-π-Bindung verhindert.

Squaraines – 1,3-substituted derivatives of squaric acid – have been known for 20 years¹⁾. Various formulations have been used to represent their structures, the most common being **1a – c**.

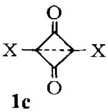


1a

(+ 3 equivalent structures)



1b



1c

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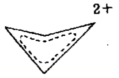
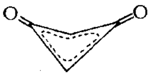
From a study of the UV and ESCA spectra of two aminosquaraines, *Neuse* and *Green*[2] concluded that squaraines are best represented by a mesoionic structure, e.g. **1a**. No ab-initio MO studies on squaraines have been reported to date.

Theoretical studies have predicted that the cyclobutadiene dication (**2a**) prefers a puckered D_{2d} geometry to the planar D_{4h} geometry expected for this Hückel 2π-aromatic system[3a]. The similar predictions for the isoelectronic 1,3-dihydro-1,3-diborete system **2b**[3b] have recently been confirmed by the *X*-ray structure determination of a derivative[3c]. Bicyclobutanedione (**3**) was also calculated to prefer a puckered structure **3a**, intermediate between the planar structure **3b** and the closed bicyclic structure **3c**[4].



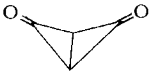
2a

2b



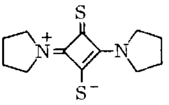
3a

3b



3c

This drew our attention to the squaraines, which can be considered as derivatives of the cyclobutadiene dication (representation **1b**) or of bicyclobutanedione (**1c**). The structures of four squaraines (**4** – **7**) have been reported previously[5–8], and **8** has been studied very recently[9]. These compounds all have a planar skeleton and thus do not exhibit the ring puckering expected for derivatives of **2** or **3**.



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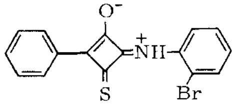

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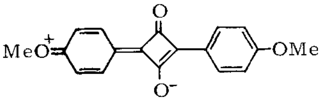

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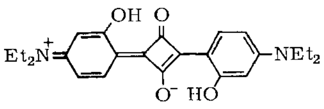

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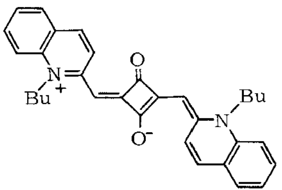

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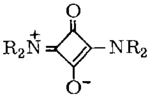


9: R_2 = $-[CH_2]_5-$
10: R = H

In this paper, we report the structure of dipiperidinosquaraine (**9**), which is also found to have a planar skeleton. In addition, we describe the results of semi-empirical and ab-initio MO calculations on diaminosquaraine (**10**) and discuss the reasons why squaraines, unlike **2** and **3**, prefer planar geometries.

The Structure of Dipiperidinosquaraine (9)

The title compound crystallizes in the orthorhombic system, space group *Pnab,* with four molecules per unit-cell. The molecule has a center of symmetry. Thus, the four-membered ring must be exactly planar; the oxygen and nitrogen atoms are very nearly coplanar with this ring. The piperidino rings have a chair conformation, and the molecule closely approximates C_{2h} symmetry, with the mirror plane passing through N, C5, H51, and H52. An ORTEP[10)] drawing of the molecule is shown in Figure 1. Important bond distances and angles are given in Table 1, and the distances to the four-

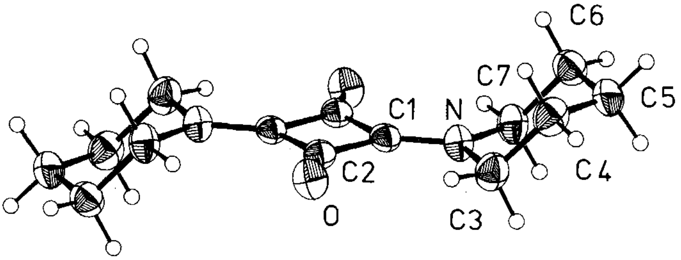


Figure 1. ORTEP Drawing of **9**, with Thermal Ellipsoids Scaled to Include 40% Probability. The Hydrogen Atoms are Represented by Artificially Small Spheres for Clarity

Table 1. Bond Distances (Å) and Angles (°) for **9**

C1−C2	1.4572(8)	C3−C4	1.503(1)
C1−C2′	1.4546(8)	C4−C5	1.507(1)
C2−O	1.2396(7)	C5−C6	1.513(1)
C1−N	1.3112(7)	C6−C7	1.511(1)
N−C3	1.470(1)	N−C7	1.463(1)
C1C2C1′	88.49(5)	C2C1N	134.12(5)
C2C1C2′	91.51(5)	C2′C1N	134.37(5)
C1C2O	135.59(5)	C1NC3	121.86(5)
C1′C2O	135.93(5)	C1NC7	122.36(5)
C3NC7	115.74(6)	C4C5C6	111.30(7)
NC3C4	110.45(7)	C5C6C7	110.62(7)
C3C4C5	111.69(8)	C6C7N	110.06(7)

Table 2. Atom-plane Distances (Å)

a) Plane through C1C2C1′C2′
N: 0.003(1) O: 0.007(1)

b) Plane through C1C1′ perpendicular to a)
N: 0.004(1) C5: 0.004(2) H51: −0.011(7) H52: −0.020(7)

c) Least-squares plane through ONC1C2C3C7 and O′N′C1′C2′C3′C7′
N: −0.014(1) O: 0.012(1) C1: −0.009(1) C2: 0.004(1)
C3: −0.006(1) C7: 0.020(1)

membered ring plane and the approximate mirror plane in Table 2. The packing of the molecules is similar to that found in dipyrrolidinodithiosquaraine (**4**)[5], and there are no short intermolecular contacts.

The C – C bonds in the four-membered ring (1.456 Å av.) are only slightly shorter than normal $C_{sp^2} - C_{sp^2}$ single bonds (1.466 Å[11]). The C – O distances (1.240 Å) are somewhat longer than normal C – O double bonds (1.215 Å[12]) but much shorter than C – O single bonds (1.426 Å[12]). Similarly, the C1 – N bonds of 1.311 Å are closer in length to double bonds (c.f. 1.273 Å in $CH_2 = NH$[13]) than to single bonds (1.472 Å[12]). Bond distances in the central part of the molecule are compared with those in **4** – **6** in Table 3 (no geometrical details have been reported for **7**[8]). Inspection of the Table shows that the four molecules have rather similar geometries which presumably reflect similar bonding relationships within the molecules. This justifies naming them all as squaraines[1] despite the large differences in donor (amino-, aryl-) and acceptor (C = O, C = S) groups.

Table 3. Bond Lengths (Å) for Squaraines

Compound	Method	av C – C (ring)	C – O	C – S	C – N	C – C (ext)	Ref.
4	*X*-ray	1.438		1.652	1.330		[5]
5	*X*-ray	1.462	1.215	1.649	1.303	1.435	[6]
6	*X*-ray	1.482	1.230			1.412	[7]
9	*X*-ray[a]	1.456	1.240		1.311		this work
10	MINDO/3	1.477	1.213		1.318		this work
10	MNDO[b]	1.479	1.224		1.345		this work

[a] These parameters were also used for the STO-3G and 3-21G calculations. – [b] D_{2h} symmetry imposed; see text.

The Bonding in Diaminosquaraine (10)

The model compound **10** was examined by ab-initio (STO-3G and 3-21G) and semi-empirical (MINDO/3 and MNDO) methods. For the ab-initio calculations, an idealized D_{2h} geometry corresponding closely to the crystal geometry of **9** was assumed. The MINDO/3- and MNDO-optimized geometries for **10** (D_{2h} symmetry assumed) have been included in Table 3.

The π-electron densities from the ab-initio and semi-empirical calculations are given in Table 4. The individual electron densities on C1, C2, N, and O cannot be interpreted easily because of polarization in the C – N and C – O bonds. However, the total π-elec-

Table 4. π-Electron Densities and (CNH_2) → (CO) Donations in **10**

Method	π-Densities				π-Donation[a]	Total Donation
	C1	C2	N	O	$CNH_2 \rightarrow CO$	$CNH_2 \rightarrow CO$
STO-3G	0.860	1.000	1.746	1.394	0.394	0.191
3-21G	0.874	0.900	1.725	1.501	0.401	0.143
MINDO/3	0.938	0.735	1.705	1.622	0.357	0.041
MNDO	0.940	0.846	1.741	1.473	0.319	0.108

[a] $(q^{\pi}_{C2} + q^{\pi}_{O} - 2) = (3 - q^{\pi}_{C1} - q^{\pi}_{N})$.

tron densities in the CNH_2 and CO units should be more significant. The ab-initio calculations show a transfer of ca. 0.4 π-electron from each CNH_2 unit to a CO unit, which is very close to the value of 0.5 *e* corresponding to representation **1a**. For the cyclobutadiene dication-like formulation **1b** one would expect a donation of 1 electron, and representation **1c** corresponds to zero transfer. However, the *net* atomic charges show that this transfer of π-electrons is largely compensated by an opposite flow in the σ-system; the *net* transfer from CNH_2 to CO is less than 0.2 electron. Thus, the charge separation in **10** is much smaller than that implied by representation **1a**.

The occupied π-orbitals and the LUMO of **10** are shown schematically in Figure 2. Only the lowest (π_1) shows an appreciable amount of C – C π-bonding. Both π_1 and π_2 are C – N π-bonding, but the HOMO (π_5) is C – N antibonding. π_1, π_3, and π_4 are all C – O bonding.

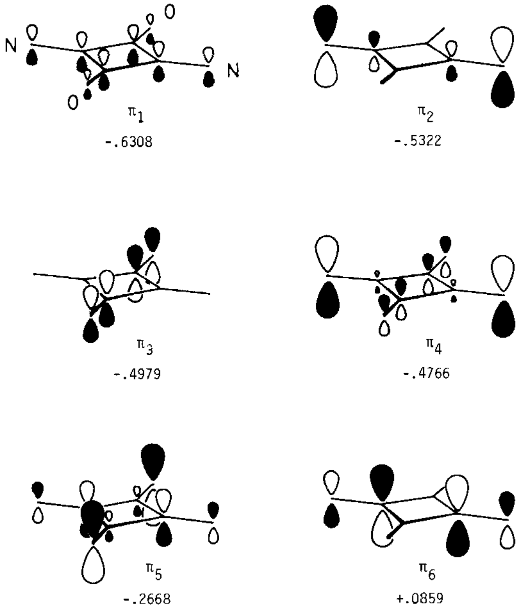
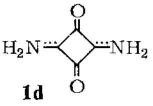


Figure 2. Schematic Representations of the Lowest 6 π-Orbitals of **10**, with their 3-21G Orbital Energies. π_5 is the HOMO, π_6 the LUMO

Figure 3 shows the STO-3G overlap populations for **10** and some reference compounds. The population analysis indicates only a small amount of C – C π-bonding. The C – N π overlap population is larger, indicating considerable C – N π-bonding, and the C – O overlap population would indicate rather more than half a π-bond. These data, the small charge separation in **10**, and the observed short C – O and C – N bonds in **9**, all suggest that diaminosquaraine (**10**) is more accurately represented by **1d**.



1d

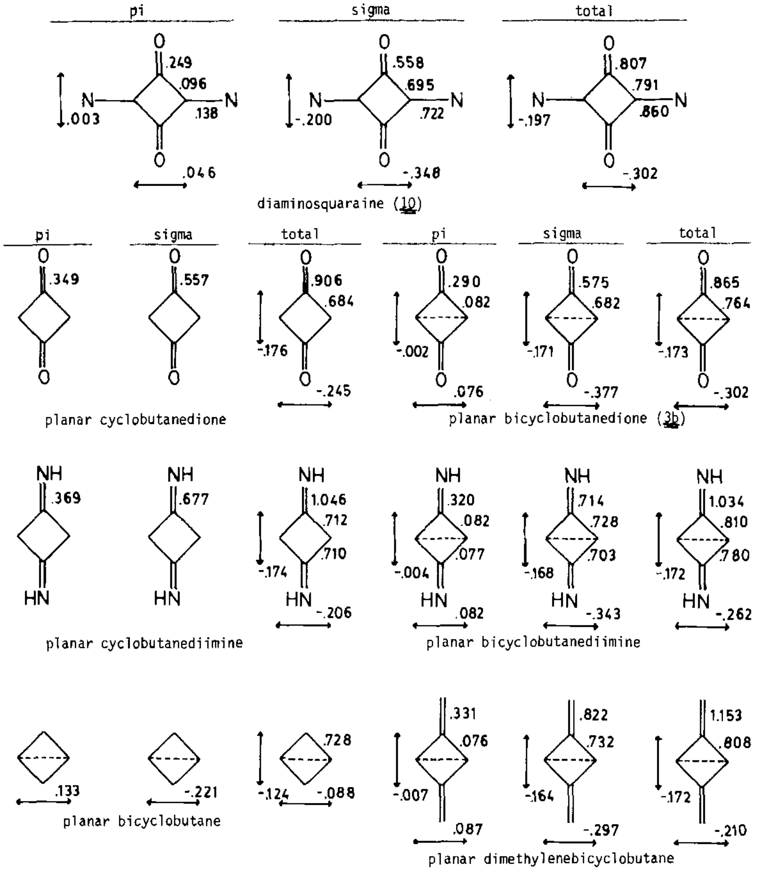


Figure 3. STO-3G Overlap Populations for **10** and Some Reference Compounds

As an added advantage, **1d** shows the high symmetry of the squaraine system much more clearly than does **1a**. A drawback is that **1d** does not show the formal electron count.

The transannular π overlap populations in **10** are small (Figure 3). In contrast, the transannular σ overlap populations are *large* and *negative*, indicating the presence of strong 1,3-repulsive interactions which are a common feature of planar 4-membered ring compounds[14]. In accord with this, a *Urey-Bradley* force constant analysis has shown the presence of strong 1,3-repulsions in the related squarate ion[15].

The geometry of **10** was optimized with the MINDO/3[16] and MNDO[17] methods. Surprisingly, planar D_{2h} **10** is not a local minimum on the MNDO potential surface. Optimization in C_i symmetry resulted in a structure which had a planar C_4O_2 skeleton with amino groups bent out of the ring plane and showing considerable pyramidalization. Clearly, MNDO underestimates the nitrogen-ring interaction; this is also apparent from the C–N bond lengths obtained with imposed D_{2h} symmetry (Table 3). MINDO/3 correctly predicts a planar D_{2h} geometry for **10** and also produces a correct

C – N bond length. This agreement may, however, be fortuitous: it is known that MINDO/3 underestimates the tendency of nitrogen to pyramidalize, and a similar underestimation of the nitrogen-ring interaction may have resulted in a cancellation of errors. In accord with this interpretation, both methods predict a C – O bond length somewhat shorter than the experimental value for **9** and nearly equal to that of a full double C – O bond.

The Planarity of Squaraines

Why do squaraines, which are formally related to the cyclobutadiene dication[3)] and to bicyclobutanedione[4)], prefer planar over non-planar structures? The calculations indicate the presence in **10** of strong 1,3-repulsive interactions which are the main factor leading to the puckering of the cyclobutadiene dication[3)]. The puckering of bicyclobutanedione, although also favoured by the alleviation of 1,3-repulsive interactions, is caused mainly by the incipient 1,3-C – C σ-bond formation[4)]. In particular, the HOMO in **3**, which is mainly located on C1 and C1′ and the oxygen atoms and is largely non-bonding in the planar structure **3b**, becomes 1,3-σ-bonding on ring puckering to **3a**. In 1,3-diaminosquaraine (**10**), C1 and C1′ are engaged in C – N π-bonding and thus are less inclined to form a C – C σ-bond. The coefficients on carbon in the HOMO of **10** are smaller than those in **3b**, the possibilities for C – C bond formation are diminished, and the energy gain associated with ring puckering would be insufficient to compensate for the loss in π overlap. The effect of π-donor substituents on the planar bicyclobutanedione system can also be seen in the π overlap populations in Figure 3. The influence of amino groups in **10** decreases the C – O- and the 1,3-C – C π-overlap populations and increases slightly the 1,2-C – C π-overlap populations with respect to **3b**. In short, the amino substituents not only stabilize a planar structure through π-donation via the carbon ring to oxygen, but also oppose ring puckering by making 1,3-σ-C – C bonding less favorable. The same arguments can be applied to squaraines bearing other types of π-donor substituents. Only squaraines with very poor donors, e.g. alkyl and possibly phenyl, are expected to prefer nonplanar structures. There are, however, indications that such compounds are extremely reactive and may be difficult to isolate and characterize[18)].

This work was supported by the *Fonds der Chemischen Industrie* and the *Deutsche Forschungsgemeinschaft*. P.H.M.B. expresses his gratitude for a Fellowship sponsored by the *Netherlands Organization for the Advancement of Pure Research* (Z.W.O.). We thank *A. H. Schmidt*, *J. Bernstein* and *R. West* for their interest.

Experimental Part

X-Ray Structure Determination of **9**[*)]: A specimen of the title compound was prepared according to a literature procedure[19)]. A needle shaped crystal, obtained by crystallization from water, was cut to approximate dimensions 0.4 × 0.2 × 0.1 mm and mounted with the needle direction ca. 30° off the axis on a glass fibre. The space group was determined as *Pnab* (D_{2h}^{16}), with four

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[*)] Further details and basic data concerning the *X*-ray analysis may be obtained from Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW, England.

Table 5. Atomic Parameters (e.s.d.'s in Parentheses). The Temperature Factors are Given by $T_{\text{aniso}} = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

ATOM	X	Y	Z	U11 OR U	U22	U33	U12	U13	U23
C(1)	.52694(7)	.57549(6)	.53673(3)	.0289(4)	.0457(4)	.0392(4)	.0032(3)	.0021(3)	-.0028(3)
C(2)	.47643(8)	.57698(6)	.46161(3)	.0306(4)	.0479(4)	.0430(4)	.0021(3)	.0011(3)	-.0035(3)
C(3)	.5563(1)	.8231(1)	.56571(4)	.0681(6)	.0468(5)	.0476(5)	-.0101(5)	-.0029(5)	.0025(4)
C(4)	.4352(1)	.90124(9)	.61756(5)	.0584(6)	.0384(5)	.0686(5)	.0035(5)	-.0019(5)	-.0039(4)
C(5)	.4907(2)	.87221(9)	.69350(5)	.0628(7)	.0477(5)	.0533(5)	-.0016(4)	.0074(5)	-.0144(4)
C(6)	.4923(1)	.71651(9)	.70888(4)	.0622(6)	.0499(5)	.0448(5)	-.0021(5)	.0069(5)	-.0003(4)
C(7)	.6175(1)	.64045(9)	.65698(5)	.0560(6)	.0492(5)	.0426(5)	.0068(5)	-.0096(4)	-.0045(4)
N	.56262(6)	.67322(4)	.58389(2)	.0501(3)	.0414(3)	.0378(3)	.0048(3)	-.0050(3)	-.0035(3)
O	.44899(5)	.66883(4)	.41611(2)	.0669(3)	.0495(2)	.0448(3)	.0078(2)	-.0064(2)	.0059(2)
H(31)	.6849(8)	.8606(6)	.5679(3)	.105(6)	.049(5)	.057(5)	.009(4)	.036(5)	-.019(3)
H(32)	.5091(9)	.8342(6)	.5164(3)	.130(6)	.021(3)	.064(4)	.004(4)	.009(4)	-.007(4)
H(41)	.4425(7)	1.0017(5)	.6070(3)	.089(5)	.033(3)	.074(4)	.019(4)	.011(3)	-.022(4)
H(42)	.3062(8)	.8733(6)	.6098(3)	.065(5)	.054(5)	.075(5)	.009(4)	.005(4)	.012(4)
H(51)	.6164(8)	.9125(6)	.7043(3)	.104(6)	.045(4)	.040(4)	.010(5)	-.003(5)	-.001(3)
H(52)	.4130(9)	.9218(6)	.7280(3)	.132(7)	.038(4)	.033(5)	-.011(4)	-.011(4)	.011(3)
H(61)	.5365(8)	.6969(5)	.7565(3)	.072(5)	.027(3)	.076(5)	.021(3)	.034(4)	.011(4)
H(62)	.3627(7)	.6783(6)	.7038(3)	.057(5)	.034(4)	.086(5)	.014(4)	.018(4)	.005(4)
H(71)	.7485(8)	.6715(7)	.6648(3)	.082(6)	.114(6)	.023(4)	.027(5)	.008(4)	-.013(4)
H(72)	.610(1)	.5383(6)	.6637(3)	.102(6)	.102(5)	.009(3)	.022(6)	.010(3)	-.012(5)

molecules in a cell of dimensions $a = 7.1798(9)$, $b = 9.5362(8)$, and $c = 18.788(2)$ Å ($V = 1286$ Å^3, $D_{\text{calc}} = 1.282$ g/cm^3). A total of 22010 reflection profiles ($2° < \Theta < 27°$) were determined at 291 K using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). Averaging yielded a unique set of 1405 structure factors, 871 of which were stronger than 2σ. The structure was solved by direct methods (MULTAN 76[20]) and refined by full-matrix least squares methods (*X*-ray 76[21]) using weights $1/\sigma^2(F_o^2)$. Neutral-atom scattering factors were taken from ref.[22]. The introduction of all hydrogen atoms with isotropic temperature factors and anisotropic thermal parameters for the non-hydrogen atoms led to quick convergence. Then all hydrogen atoms could also be refined anisotropically (we plan low-temperature measurements with the substance, since the crystals seem to be suitable for an electron-density study). The final R values, based on the 871 $F_o^2 > 2\sigma$, reduced to $R(F^2) = 0.059$, $R_w(F^2) = 0.043$. The highest peak in the final difference Fourier was 0.27 e/Å^3. The final atomic coordinates and thermal parameters are given in Table 5.

Theoretical Procedures: Restricted Hartree-Fock calculations[23] on **10** using the minimal STO-3G basis set[24a] and the split-valence 3-21G basis set[24b] were carried out with the GAUSSIAN-82 program[25]. The most important parameters of the structure assumed for **10** have been given in Table 4; the remaining values are: N – H = 1.000 Å, CNH = 122.0°, C1C2C1' = 88.5°.

MINDO/3[16] and MNDO[17] calculations were carried out with the MOPAC program package[26]. MINDO/3 geometry optimization of **10** in C_i symmetry produced the D_{2h} structure given in Table 3. A similar geometry optimization with MNDO produced a less symmetrical structure with approximate C_{2h} symmetry. In order to allow a comparison with the MINDO/3 structure for **10** and the experimental structure for **9**, the geometry of **10** was also optimized in D_{2h} symmetry using MNDO. The values in Table 3 correspond to the D_{2h} structure; the C_{2h} structure has slightly longer C – N distances (by 0.016 Å) and amino groups which are bent out of the ring plane by 5.5° showing appreciable pyramidalization (sum of angles around N = 344.4°).

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